SEMI-ANNUAL REPORT

OF

SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

LONDON * NEW YORK

APRIL 1912.
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<td>195</td>
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## List of abbreviations.

- \(d\) = specific gravity.
- \(d_{20}^{\circ}\) = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
- \(d_{10}^{\circ}\) = specific gravity at 20°, compared with water at 4°.
- \(a_{D}^{20}\) = optical rotation at 20°, in a 100 mm. tube.
- \([a]_D\) = specific rotation.
- \(n_D^{20}\) = index of refraction at 20°.
- Sol. p. = solidifying point.
- M. p. = melting point.
- B. p. = boiling point.
- \(n\) = normal.
- Acid v. = acid value; ester v. = ester value; sap. v. = saponification value.
- g. = gram; cc. cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.
The development of German industry — especially in our own branch of Chemistry —, has made further important progress in the year 1911, and the decided strengthening of the commercial situation which has now been noticeable for two years has stamped upon the past twelvemonth, as upon that which preceded it, the imprint of an allround wholesome and satisfactory economic period. The general retrospect would doubtless have been more favourable still if the close of the commercial year had not been seriously disturbed by difficulties and complications in foreign politics, complications of which in some instances the full extent could only be surveyed after they had been removed. The negotiations concerning Morocco, which gave rise to all manner of grave apprehensions for the relations between Germany and France, the acute tension, in the course of the autumn, between Germany and Great Britain, the Italian war with Turkey, which might easily have led to serious disturbance of the peace of Europe, and finally the troubles in China and in Persia were incidents which at times called forth a certain feeling of nervousness which affected the whole commercial life of Germany, and this of course was not without its effect upon the development of trade and industry. To these disturbing elements must be added the general rise in food-prices (partly the result of abnormal climatic conditions), which seriously impaired the purchasing-power of the whole nation, especially during the second half of the year, while the chronic labour-unrest also exercised a paralysing effect upon the spirit of enterprise in many branches of industry. In respect of the last-named feature we fully endorse the following passage in the Report of the Hamburg Chamber of Commerce: "These conditions not only weigh heavily upon German industry as a permanent danger; they also impede its further extension and development, and afford fresh proof of the necessity of closer union between the work-givers with the object of defending themselves against an aggression which is becoming well-nigh insupportable". It is true that during the past year Germany has happily remained free from great strike-movements, but it is evident that labour-disturbances such as those which have been experienced in France, and such as the coal-strike in Britain, which for several weeks

1) The introduction to the present Report and the Commercial part were written during March.
paralysed the whole industrial life of this neighbour-country, must indirectly also injure German industry. When in a country like England, which is such an important market for German products, business is practically at a standstill during a longer or shorter period, it is obvious that our export-trade cannot remain unaffected. In the German coalfields, unfortunately, the British coal-strike has also provoked disturbances, which, however, have subsided more quickly than those across the North Sea.

The strength of the German money-market was put to a severe test last autumn, when the uncertain political situation resulted in the sudden withdrawal of funds due to French and British creditors. The sensational reports, partly maliciously inspired, which appeared in certain foreign papers at the time were powerless to shake our money-market, notwithstanding the fact that simultaneously it had to meet increasing claims on the part of German traders, and the success with which it stood the trial has decidedly increased foreign respect for the financial power of Germany.

The foreign trade of the German Empire in the year 1911 shows the following totals: —

Imports 9544,8 million Marks, compared with 8930,0 million Marks in 1910,
Exports 8111,8 " " " 7474,6 " " " 1910.

A comparison between the values of the imports and exports of the three principal commercial countries of Europe bears eloquent witness to the satisfactory development of Germany's foreign trade. The figures for the years 1910 and 1911, in million Marks, were as follows: —

\[
\begin{array}{c|c|c|c|c}
\text{Germany} & \text{Exports in 1911} & 8111,8 & \text{Imports 1911} & 9544,8 \\
& \text{1910} & 7474,6 & \text{1910} & 8930 \\
& + & 1242 & & \\
\text{United Kingdom} & \text{1911} & 9222, & \text{1911} & 13815 \\
& \text{1910} & 8737, & \text{1910} & 13769 \\
& + & 531 & & \\
\text{France} & \text{1911} & 4938, & \text{1911} & 6529 \\
& \text{1910} & 4988, & \text{1910} & 5739 \\
& + & 740 & & \\
\end{array}
\]

Closer consideration of the above figures shows that the foreign trade of Germany has grown at a materially higher rate than that of either Britain or France. A surprising fact is the notable drop in French exports, the increased trading-turnover of the Republic being entirely due to the rise in imports. We should be exceeding our scope were we, in these pages, to trace the causes that have brought about a result which is the more noteworthy in view of the enactment in the year 1910 of increased protective duties, from which another outcome would certainly have been expected.

The German chemical industry, and in a more restricted sense the industry of essential oils, essences and artificial perfumes, has had its
full share of the advance in German export trade and, as will be seen from the figures given below, our branch has no cause for dissatisfaction with the results achieved:

**German foreign trade in essential oils**

<table>
<thead>
<tr>
<th></th>
<th>Imports</th>
<th>Exports</th>
</tr>
</thead>
<tbody>
<tr>
<td>1911</td>
<td>1 251 500 klos</td>
<td>599 300 klos</td>
</tr>
<tr>
<td>1910</td>
<td>1 524 300</td>
<td>547 600</td>
</tr>
<tr>
<td>1909</td>
<td>755 800</td>
<td>512 600</td>
</tr>
<tr>
<td>1908</td>
<td>911 300</td>
<td>390 800</td>
</tr>
<tr>
<td>1907</td>
<td>1 498 600</td>
<td>491 700</td>
</tr>
</tbody>
</table>

**German foreign trade in artificial odoriferous substances**

<table>
<thead>
<tr>
<th></th>
<th>Imports</th>
<th>Exports</th>
</tr>
</thead>
<tbody>
<tr>
<td>1911</td>
<td>17 300 klos</td>
<td>492 800 klos</td>
</tr>
<tr>
<td>1910</td>
<td>17 900</td>
<td>428 800</td>
</tr>
<tr>
<td>1909</td>
<td>16 100</td>
<td>417 100</td>
</tr>
<tr>
<td>1908</td>
<td>11 300</td>
<td>280 000</td>
</tr>
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</table>

It will be seen from these statistics that the imports of essential oils as well as of artificial odoriferous substances have fallen off in a not inconsiderable degree, while it is satisfactory to note that the exports of the former have risen by over 50,000 klos and of the latter by as much as 64,000 klos. The German artificial perfume industry has a right to be particularly proud of this result, because it has been achieved in a branch in which foreign, and especially Swiss, competition is extremely keen. As in previous years so in 1911 a very important share of the total imports of essential oils falls to the account of our firm. Our receipts of camphor oil alone amounted to about one-fourth of the entire imports.

In point of fact our business during the past year has been marked by a steady and healthy increase in turnover, and by such briskness in almost every consuming market that from the very commencement of the year, and in spite of the incidents which, as stated above, disturbed the course of trade at intervals, a favourable financial result appeared to be assured. The already excellent demand for our manufactures in almost all consuming markets was further assisted by the rising tendency of certain important articles, such as menthol, sandalwood oil and — towards the close of the year — the Italian essences, with the result that our business developed to such a degree as to throw completely in the shade even the record year 1907. We certainly have no cause to draw other than a most favourable picture of our operations in the year 1911, and we are convinced that every firm in our branch of industry which

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1) Statistisches Warenverzeichnis No. 353 b/c.
2) Statistisches Warenverzeichnis No. 354.
has built up its business on the same sound principles that govern ours will have had a similar satisfactory experience.

The first two months of the present year have also been characterised by an animated demand and an increasing turnover, and there is every prospect of continued favourable development, provided peace be maintained. By increasing the number of steam-boilers in our works to 23, with an aggregate heating-area of 2500 sq. meters, we have prepared ourselves for a further expansion of our output, after having been compelled to raise our capacity of production to its highest power, by introducing the day- and night-shift system in some of our principal departments, thus securing continuous working.

Before passing to our customary detailed review of the various markets we are compelled, to our regret, to record the disagreeable fact that during the past year the malpractice of adulteration has attained dimensions never previously known in our branch. Perhaps the most eloquent testimony on this subject is afforded by the numerous occasions on which our testing-laboratory has been asked to pronounce an expert-opinion. The alarming extent to which the ever-advancing scientific investigation of the constituents of the essential oils is utilised by dishonest traders to practise cunning forms of adulteration, especially such as are designed to represent their goods as of better quality than they really are, is positively astounding. In the great majority of cases the primary methods of examination, as for instance the determination of specific gravity, of solubility and of optical rotation, and even the simpler chemical tests, such as saponification and acetylation, no longer suffice to trace malpractices of this kind, and it is necessary to carry out the various investigations in all their complicated details in order to reveal the inferior nature of the artificial mixtures. We regard it as a particularly painful matter that firms should be found which are not ashamed openly to offer for sale preparations that appear to be suitable for the manufacture of such ingenious sophistications, and to offer them on the express ground that the preparation serves some such purpose as that of apparently increasing the ester-content of an oil. We have on previous occasions quoted several instances of this practice, which is carried on sometimes by letter and sometimes through travellers. That German firms should take part in such a traffic is the more deplorable because it has been one of the chief merits of the German research-chemists that for many years they have successfully laboured to raise the whole of the essential oil trade to a higher level by establishing suitable methods of examination, and it must be obvious that for us, who have been pioneers in this field of research, the existence of such malpractices must be particularly unpleasant. Quite recently we were informed of a case in which a German firm which makes pretensions to rank among the first and most important in the chemical industry was offering in various places abroad preparations of which the
purpose is fictitiously to increase the ester-content of essential oils. The letter in which the offer was made was sent to us; the name of the preparations we suppress in the interest of honourable trading. We hope that the repeated discovery by us of such regrettable incidents will at length bring about a change in this state of things, for in the alternative we shall certainly take an early opportunity of publicly pillorying the firms concerned, whose original offers are in our possession.

A word, also, on the subject of the deplorable cases of methyl alcohol poisoning. We have always advocated the view that the employment for purposes of human consumption of this substitute for ethyl alcohol is unjustifiable, but we have also repeatedly pointed out that there are grave objections to its use in the manufacture of perfumes and cosmetics, notwithstanding the fact that these articles are for external use only. We know that important methyl alcohol manufacturers are in the habit of recommending their preparation for the last-named purposes, and in order to guard our business-friends against unpleasant experiences we expressly warn them not to entertain such suggestions.

Our Branch-Office at Bodenbach has obtained its well-deserved share of last year's business-successes, our sales in the Austro-Hungarian Monarchy showing a considerable increase. In the spirits-department, however, the conditions were far from favourable, for to the burdens and obstructions which have beset this branch of trade in the past few years there is now to be added the Spirit-Trust, while the threatened Spirit Taxation Bill contributes to render the situation far from rosy. Operations have been started in the meantime in the extension of our Bodenbach works, to which we have already referred on a previous occasion, and among other processes of manufacture we have commenced the preparation on a large scale of sugar-colour from refined sugar. We take this opportunity of again calling the attention of our Austrian and Hungarian friends to this article.

Our relations with our customers in France have developed in a highly satisfactory manner, in spite of the increased Customs Duties imposed in 1910, which so seriously hamper the importation of our products. German exports to France in the year 1911 showed an increase in value of over 88 million Marks, and although it need scarcely be said that the share of our branch of industry in this increase is a very modest one, we are pleased to be able again to place upon record the steady and wholesome expansion of our relations with our Western neighbour. The political tension, which last autumn might easily have led to a catastrophe, has again given place to a more amicable disposition, except as regards a persistently Chauvinistic section of the French press, and there is no cause for believing that the prospects of a return of restful conditions and mutual confidence, even in a political sense, are unfavourable. The demand from France last year was not limited chiefly to those costly
artificial perfumes which give their characteristic stamp to so many French perfumery-specialities, but all other articles of our manufacture were likewise in strong request. The troubles with the Custom-House, to which we have already previously referred, still persist, although here, too, it cannot be gainsaid that there has been some improvement.

Our turnover in Great Britain has again experienced a marked increase in 1911, our London branch having been fully occupied throughout the year. In view of the many vexations that have beset trade in this country in the past year this result must be regarded as thoroughly satisfactory, the more so because a state of political and economic quiescence, such as is imperative to salutary commercial development, appears unfortunately, so far as Britain is concerned, to belong to the realm of the future. Apart from the state of political tension, sedulously fostered by a section of the press both in Germany and in the British Isles, which in the second half of 1911 was at times so great as to give rise to fears of a rupture between the two nations, and of which the after-effects are unfortunately not yet wholly dispelled, the internal political imbroglio, to which reference has already been made on previous occasions, is by no means cleared up. The Irish Home Rule question continues to excite the minds of the people and makes it difficult for Parliament to settle down to quiet work. There is no doubt that this state of things will persist until this vexed question has been disposed of in some way or other. To this must be added the strikes which are forever breaking out in fresh places, and among which the gigantic national colliers' strike which broke out in the beginning of March constitutes the record, inasmuch as it involved the voluntary cessation from work of a million coal-miners, and has drawn into common suffering nearly 600000 workers in other industries, because the factories which employed them had to close down for lack of coal. Although the end of this calamity is now at hand, the wounds inflicted by such a national catastrophe are far less easily healed than given. Hence the prospects for the immediate future could hardly be regarded as rosy were it not that Britain's powerful financial position in the world's commerce is a favourable factor which must not be under-estimated. Notwithstanding all the great internal difficulties of the country the trade statistics continue to show steadily increasing imports and exports (see p. 6).

With regard to trade with British India there is, generally speaking, little or no news to be reported. The turnover increases within normal limits, but this vast, although proportionately poor, market is only slowly beginning to recognise that the buyer who is everlastingly seeking to buy low-priced goods will usually find, on examining his purchase and comparing its value, that he has made a thoroughly bad bargain. Over and over again we encounter quotations which show only too clearly the kind of rubbish to which "cheap competition" has accustomed the native trader, who very often is a most credulous person and possesses only the most
superficial acquaintance with the means of judging the value of goods in our branch of industry. To this must be added the unsound practice by which indents from India to European export-houses are almost invariably placed on the basis of price alone, that is to say, unless special sources of supply are indicated, the export-firm concerned simply sends round a request for "lowest quotations" to a dozen or so of manufacturers, and he who quotes least obtains the order. It is evident that under such conditions British India is bound to become the staple-place for rubbish of all descriptions, and European firms in that country have already denounced this state of things in the press without stint. But even here daylight is breaking, and we are glad to be able to state that the better elements among the traders and consumers have become much more appreciative of first-class, pure qualities than was the case a few years ago. But a great deal of pioneering-work still needs to be done to bring consumers at large to a sense of the importance of pure wares.

The Coronation-Durbar, which was celebrated with enormous pomp and a truly Oriental gorgeousness, has passed off without untoward incidents. The elevation of Delhi to the rank of the Capital of India was the most important episode of these festive days. This step, the sequel of conditions of which the discussion lies outside our scope, was entirely unexpected, and naturally created an unpleasant impression in Calcutta, the present Capital. But it would appear that city has quickly accommodated itself to the new order of things, for although it may be loath to be deprived henceforth of the splendour of the splendour of the Vice-Regal Court, that removal cannot depose it from its place as the chief commercial centre of British India.

The craze for cheapness, to which we referred above, also remains an unfavourable factor in business-relations with Australia. It is true that things are not quite so bad here as they are in the Indian trade, but it needs continuous exertion on the part of respectable firms successfully to combat this deep-seated evil, especially because an inevitable result of such traffic is that the goods supplied are invariably of low quality, and bound sooner or later to disappoint the buyer bitterly. This fact, although it should be self-evident, cannot too often be brought to the notice of those buyers whose one and only guide is lowness of price, who regard the test of quality as a matter of subordinate concern, and who, in fact, consider it almost their duty invariably to prefer the lowest quotation. For the rest there is nothing new to report concerning Australian trade, the turnover being steadily although slowly on the increase. The economic conditions upon which we commented in our last Report apparently continue to hamper the normal development of the entire Continent; a fact which is readily understood by those who known Australian conditions from personal observation. The disinclination of large capitalists to invest money in new industrial undertakings in that country while these
conditions prevail scarcely requires comment: one can only express regret that the development of this highly-promising and otherwise prosperous land should be retarded by such artificial checks as have been imposed there during the past decade or so.

There has been very little alteration since last autumn in the economic condition of Spain. The bad harvests of 1909 and 1910 have been followed in 1911 by good, and in parts even excellent, crops, especially of wine and oil, but the effect of these is hardly perceptible owing to the critical state of Spanish politics. In the first place the Morocco-adventure, of which the end seems to be far distant, is always calling for fresh sacrifices of life and gold. The Liberal party still holds the reins of Government, but such difficulties have been thrown in the path of the Prime Minister by the Conservatives that he has twice offered his resignation since last Autumn, and has only been induced to continue at his post by the personal intervention of the King. Naturally, such an unsatisfactory state of things is not exactly conducive to the revival of trade and industry. In spite of this both the imports and exports have increased during the past decade, as will be seen from a comparison of the figures for the years 1900 and 1909 which we quote from an article in the Heraldo de Madrid. Statistical data of Spanish commerce are somewhat scarce, and we give an abstract of the article in question, because the figures give an approximate idea of the facts. They show that the direct export trade from Germany to Spain has increased between 1900 and 1909 by 36 700 000 Pesetas, or nearly 50%. In connection with this it must be remembered that large quantities of German goods are imported by way of other countries, especially France and Great Britain, and appear in the statistics as French or British goods.

<table>
<thead>
<tr>
<th>Pesetas</th>
<th>Imports from:</th>
<th></th>
<th>Exports to:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1900</td>
<td>1909</td>
<td>1900</td>
<td>1909</td>
</tr>
<tr>
<td></td>
<td>Million</td>
<td>Million</td>
<td>Million</td>
<td>Million</td>
</tr>
<tr>
<td>Germany</td>
<td>77,8</td>
<td>114,5</td>
<td>31,9</td>
<td>48,4</td>
</tr>
<tr>
<td>France</td>
<td>147,4</td>
<td>198</td>
<td>217,3</td>
<td>238,9</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>249,3</td>
<td>206,2</td>
<td>276,8</td>
<td>267,1</td>
</tr>
<tr>
<td>Belgium</td>
<td>43</td>
<td>32,2</td>
<td>25,3</td>
<td>36,2</td>
</tr>
<tr>
<td>Portugal</td>
<td>41,9</td>
<td>48,2</td>
<td>36</td>
<td>48,4</td>
</tr>
<tr>
<td>Russia</td>
<td>42,6</td>
<td>26,3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Italy</td>
<td>24,2</td>
<td>93,9</td>
<td>24,4</td>
<td>42,6</td>
</tr>
<tr>
<td>Holland and the rest of Europe</td>
<td>74,3</td>
<td>42,2</td>
<td>88,1</td>
<td></td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td><strong>700,5</strong></td>
<td><strong>719,3</strong></td>
<td><strong>653,9</strong></td>
<td><strong>769,7</strong></td>
</tr>
<tr>
<td><strong>Increase:</strong></td>
<td>about 3%</td>
<td></td>
<td>about 17,5%</td>
<td></td>
</tr>
</tbody>
</table>

Statistical data of Spanish commerce are somewhat scarce, and we give an abstract of the article in question, because the figures give an approximate idea of the facts. They show that the direct export trade from Germany to Spain has increased between 1900 and 1909 by 36 700 000 Pesetas, or nearly 50%. In connection with this it must be remembered that large quantities of German goods are imported by way of other countries, especially France and Great Britain, and appear in the statistics as French or British goods.
The U. S. Consul at Malaga\(^1\) reports that about twelve years ago the preparation of essential oils was taken up there, and although, judging by the value of the output, the business is one of the less important of the new branches of industry which have arisen in the locality, it is apparently one of the most successful and promising. There are at Malaga five works engaged in the preparation of essential oils, and two of these have been equipped with up-to-date steam-distilling plant and are managed by German chemists. The whole of the output is exported, and all the processes of distilling, hand-pressing and "enfleurage" are carried out on strictly scientific lines. The industry is remarkable for the variety of its productions, among which are the following: oils of anise, lemon, geranium, neroli, pennyroyal, rosemary, spike, red thyme and juniper. Although herbs and flowers for the preparation of essential oil are very little grown, there is no scarcity of raw material, and distilling can be carried on all the year round.

The local custom-house statistics show that the productivity of the chemical industry of the district has grown considerably within the past three years. In the year 1908 the exports amounted to about 38260 kilos, in 1909 to 89800 kilos, and in 1910 to as much as 145130 kilos. The principal part of the exports is absorbed by France, Germany, Great Britain and Cuba. Artificial essential oils are also being prepared on a small scale.

Russia, which is an important consuming-market for our articles, affords no occasion for special comment. It is only necessary to call attention to the fact that in this country competition is very keen, and is not always conducted on honourable lines.

There is nothing of material importance to record with regard to business in the Balkan-States. Roumania is steadily developing into a market for our manufactures which is worthy of serious attention, and the conditions of credit in this country have ameliorated; confidence in Turkey, on the other hand, will not be fully restored until the regrettable war with Italy has come to a termination. Unfortunately there is at present no sign of this. According to the *Reichs-Gesetzblatt*, the official Gazette of Germany, the Commercial Treaty between Turkey and Germany of 26\(^{th}\) August 1890, and the Supplementary Agreement of 25\(^{th}\) April 1907 belonging to that Treaty, both of which were due to expire on March 13\(^{th}\), have been provisionally extended by mutual agreement until 24\(^{th}\) June 1914. In Servia there has been a very gratifying development in the sale of articles of our branch, and the knowledge necessary for the proper appreciation of our standard of quality is gradually making way there. We quote from the *Chemische Industrie*\(^2\) the following brief particulars concerning the business in essential oils and perfumes in Servia in the

\(^{1}\) Daily Consular and Trade Reports, 10. 2. 1911.

\(^{2}\) Chem. Industrie 85 (1912), 83.
year 1910: The value of the imports of articles falling under this heading in 1910 was 219519 Dinars, compared with 152888 Dinars in 1909. The articles themselves included: essential oils from wood tar and rubber (?), resin oil, spirits of resin, turpentine oil and camphor oil, together 65763 kilos, valued at 42337 Dinars, of which 50614 kilos came from Russia and 12423 kilos from Austria-Hungary; essential oils of juniper, laurel, jasmine, almond, rosemary and bergamot, together 12736 kilos, valued at 14187 Dinars, all of which was imported from Germany; fine essential oils of rose, lily of the valley, violet and orange-flowers, valued at about 25000 Dinars and also imported from Germany; artificial perfumes, of which the importation is small, also from Germany. Of perfumery 5936 kilos, valued at 59946 Dinars, were imported almost entirely from Germany; various cosmetics (6165 kilos, valued at 56804 Dinars) came from Germany (3481 kilos) and France (1927 kilos). It will be seen from these figures that the sale of articles of our branch in Servia has developed quite satisfactorily.

Nothing remains to be said in the present Report with regard to the other European markets.

The position of affairs in Egypt is rather less favourable than last year, for this country is primarily dependent, for good or evil, upon its harvest. According to the Customs Statistics the cotton-crop of 1910/11 has yielded a return of £ 26550000, whereas the estimated export-value of the 1911/12 crop is only £ 19500000. Such a falling-off must be the heavier to bear because the country has not yet quite recovered from the crisis of 1907. As a result the conditions of credit once more leave a great deal to be desired at present. According to a report published by the German Ministry of the Interior¹) the fact should be borne in mind that Egypt itself has been unable to provide the capital required for the rapid growth of her economic life during the past decade, and has been mainly dependent upon foreign credit. If, therefore, the process of restoration to economic health is to take a normal course it is of prime importance that this credit should not be shaken, and especially that with the moderate crop of the present year the credits should be renewed until the gathering of the new crop.

The Bulletin of the French Chamber of Commerce at Alexandria²) publishes an interesting article on the importation into Egypt of toilet-preparations and perfumes. We reproduce this article below in the expectation that it may convey useful hints to some of our friends engaged in the perfumery-industry.

According to statistical returns, the imports into Egypt of powders, cosmetics, extracts, toilet-waters and face-paints during the past seven years have reached an average value of £ 44000, of which one-half falls

to the share of France. There is no doubt that this figure does not represent the actual value of the consumption, for the leading druggists and pharmacists in the large centres of Cairo and Alexandria generally prepare their own Eau-de-Colognes and toilet-waters, mouth-washes, dentifrices and scents, especially because by doing so they are able to supply at much lower prices. Hairdressers, likewise, rarely use articles prepared in Europe; they lay in their requirements for the most part from the native druggists, or they prepare them themselves. The extremely low cost of alcohol explains this practice, for it enables the natives to manufacture the goods more cheaply than they could buy them ready-made. From Britain the principal imports in this branch consist of Eau-de-Cologne, cosmetics, hair-restorers and tooth-pastes. English perfumes, on account of their costliness, are only used to a small extent, chiefly by Europeans.

<table>
<thead>
<tr>
<th>Country</th>
<th>1903</th>
<th>1904</th>
<th>1905</th>
<th>1906</th>
<th>1907</th>
<th>1908</th>
<th>1909</th>
</tr>
</thead>
<tbody>
<tr>
<td>Great Britain</td>
<td>4,393</td>
<td>5,022</td>
<td>4,558</td>
<td>4,946</td>
<td>4,776</td>
<td>4,984</td>
<td>6,467</td>
</tr>
<tr>
<td>Germany</td>
<td>8,138</td>
<td>8,622</td>
<td>6,916</td>
<td>5,919</td>
<td>7,077</td>
<td>4,949</td>
<td>4,687</td>
</tr>
<tr>
<td>Austria-Hungary</td>
<td>1,508</td>
<td>2,966</td>
<td>2,261</td>
<td>2,012</td>
<td>2,918</td>
<td>1,061</td>
<td>860</td>
</tr>
<tr>
<td>Belgium</td>
<td>112</td>
<td>188</td>
<td>87</td>
<td>127</td>
<td>141</td>
<td>141</td>
<td>196</td>
</tr>
<tr>
<td>China and Eastern Asia</td>
<td>402</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>U. S. America</td>
<td>785</td>
<td>1,271</td>
<td>1,096</td>
<td>1,343</td>
<td>1,709</td>
<td>1,448</td>
<td>991</td>
</tr>
<tr>
<td>France</td>
<td>19,790</td>
<td>23,073</td>
<td>21,566</td>
<td>29,452</td>
<td>33,638</td>
<td>24,179</td>
<td>25,059</td>
</tr>
<tr>
<td>Greece</td>
<td>41</td>
<td>83</td>
<td>245</td>
<td>313</td>
<td>332</td>
<td>168</td>
<td>298</td>
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<tr>
<td>Holland</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Italy</td>
<td>667</td>
<td>847</td>
<td>617</td>
<td>771</td>
<td>1,421</td>
<td>792</td>
<td>941</td>
</tr>
<tr>
<td>Russia</td>
<td>—</td>
<td>44</td>
<td>21</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Switzerland</td>
<td>13</td>
<td>19</td>
<td>—</td>
<td>17</td>
<td>—</td>
<td>36</td>
<td>54</td>
</tr>
<tr>
<td>Turkey</td>
<td>2,182</td>
<td>2,642</td>
<td>2,683</td>
<td>2,635</td>
<td>3,104</td>
<td>3,158</td>
<td>2,913</td>
</tr>
<tr>
<td>Other countries</td>
<td>15</td>
<td>—</td>
<td>52</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Total</td>
<td>38,047</td>
<td>44,777</td>
<td>40,102</td>
<td>47,894</td>
<td>55,116</td>
<td>40,916</td>
<td>42,490</td>
</tr>
</tbody>
</table>

and by natives of high rank. German perfumes were unknown in Egypt 25 years ago, but to-day Germany supplies one-tenth of the total imports. The German manufacturers have not only appointed local agents, but they work the whole country systematically by commercial travellers and thus gradually increase their sales year by year. The high-water mark of German imports, however, was reached in the years 1903 and 1904. From that time until 1909 it fell by 50% in favour of French preparations, which have everywhere replaced the competing German articles. German goods mostly go to the Arab consumers in the villages and towns; they consist of attractive but cheap wares of all sorts and descriptions, but especially of Eau-de-Cologne, lavender-water and preparations for the mouth and teeth. The imports from the United States in the year 1892 reached a value of over £2000; but this figure was not maintained and in 1909 the
value of imports from this quarter had fallen to £ 991, consisting mainly of Florida water, hair-restorers and a few extracts. The table below shows the proportionate shares of the various countries interested in the import trade for the years 1903 to 1909, the figures being given in £ sterling. The report suggests that the best way to secure a foothold in the Egyptian perfumery-market is to make a thorough canvass of the customers by commercial travellers, who should call on the buyer again and again. In order to reduce the expense of this method of procedure it is desirable to appoint travellers who represent several firms. The principal customers are druggists, pharmacists, jewellers, hairdressers and bazaars. As advertising is not expensive, this method of propaganda is also to be recommended, especially because the advertisements in the daily papers are read. The best seasons for travelling are September-October and March-April.

Our New York friends report on the business in the United States as follows:

"The general prospects for business in 1912 cannot be pronounced as very promising. Labor troubles, trust prosecutions, presidential election and the apprehension of quite radical changes in the Tariff, all constitute a menace to the quiet and normal development of trade. True enough, we have the labor troubles in common with Europe, but they assume a more passionate and uncurbed character here on account of the almost fanatic attitude of the labor unions against the capitalistic interest. In Europe the disturbing factors may lie more in the complications resulting from frictions in the foreign policy, here the instability of our interior conditions causes unrest and anxiety.

The Overman Bill, to which we referred in our last Report, and which in fact is equivalent to a radical revision of Schedule A (chemicals and drugs) has passed the House of Representatives by a Democratic vote of 179 against 127 dissenting Republicans and is now before the Senate. Here the Bill will be referred, in the routine way, to a committee which will hold the customary public hearings. These will serve the purpose of delaying any decision beyond the term of the presidential election, as it is absolutely unlikely that any political body would be willing to assume the responsibility for such a decisive measure and compromise itself during a presidential campaign.

The final fate of the Bill, which if adopted would seriously affect our line of merchandise, will then depend upon the composition of the new Legislature, but there is little probability that the principle underlying the present Bill, to levy duties upon raw materials, while reducing the rates upon manufactured articles at the same time, will ever be adopted by a majority of both Houses.

Though serious complaints are coming forth from several branches of industry, evidently due to the tinkering with the Tariff and the above
mentioned labor troubles, there is no reason for complaint in our line of business.

The year 1911 has again brought a very considerable increase in the volume of our business over the preceding year and, though on account of keen competition, the margin of profit did not grow in the same proportion as the volume of business, the year must, nevertheless, be pronounced as a very successful one.

Referring to the business prospects for the current year and judging from the amount of contract business closed during the first months of 1912, all indications would again point to a substantial gain over the good results attained in the preceding year.

The unfavorable crop conditions for many of the important raw materials affecting our line, rendered the business during the Fall and Winter months of 1911 and 1912 rather troublesome and unprofitable, as the extremely high prices for oils of lavender, geranium and bergamot, for instance, interfered seriously with the traffic in these staple commodities.

In regard to our trade with the Dominion of Canada, the expectations expressed in our last Report with reference to the Reciprocity Bill were not fulfilled. This apparently disappointing outcome, however, did not interfere with a further satisfactory development and extension of our business in this rapidly growing territory, which affords a constantly increasing outlet for goods in our line.

We consider the policy of our business to which we have adhered during a period of over forty years, and which has been practically sanctioned by the enactment of the Pure Food Law, as the sound foundation upon which we expect to further build and enlarge our business by continuing to advocate the use of pure products in preference to cheaper and adulterated goods.”

The usual table supplied to us by our friends showing the exports from and imports into the United States of essential oils, will be found on p. 18.

The conditions prevailing in Mexico are the reverse of cheerful, but it is not difficult to understand why it is that this market, in which up to the present our goods have been able to boast an increasing sale, has not shown the expected further development last year. It cannot be denied that the failure of General Reyes’ counter-revolution has somewhat alarmed the feelings of the people, but the danger from this movement had hardly been averted when a new trouble arose which previously had attracted scarcely any attention. This is the steady growth of brigandage, which, having been allowed to go undisturbed in its commencement, has now become a formidable danger to the country, the States adjoining the Federal District, and lying therefore at the very gates of the capital, being the most infested. Up to the present all the efforts of the Government
Value of imports and exports of essential oils into and from the U.S.A. in the second half-years of 1911 and 1910.

<table>
<thead>
<tr>
<th></th>
<th>Imports</th>
<th></th>
<th>Exports</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1911</td>
<td>1910</td>
<td></td>
<td>1911</td>
</tr>
<tr>
<td>July</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duty-free</td>
<td>165,038</td>
<td>147,970</td>
<td>Peppermint Oil</td>
<td>9,190</td>
</tr>
<tr>
<td>Dutiable</td>
<td>66,848</td>
<td>47,281</td>
<td>Other indigenous oils</td>
<td>32,323</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Foreign oils, duty-free</td>
<td>3,709</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dutiable</td>
<td>7,746</td>
</tr>
<tr>
<td>August</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duty-free</td>
<td>196,190</td>
<td>150,607</td>
<td>Peppermint Oil</td>
<td>25,864</td>
</tr>
<tr>
<td>Dutiable</td>
<td>53,467</td>
<td>60,037</td>
<td>Other indigenous oils</td>
<td>24,636</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Foreign oils, duty-free</td>
<td>1,021</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dutiable</td>
<td>5,711</td>
</tr>
<tr>
<td>Sept.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duty-free</td>
<td>139,037</td>
<td>110,378</td>
<td>Peppermint Oil</td>
<td>74,193</td>
</tr>
<tr>
<td>Dutiable</td>
<td>56,127</td>
<td>36,999</td>
<td>Other indigenous oils</td>
<td>27,083</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Foreign oils, duty-free</td>
<td>2,877</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dutiable</td>
<td>2,839</td>
</tr>
<tr>
<td>October</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duty-free</td>
<td>164,169</td>
<td>130,909</td>
<td>Peppermint Oil</td>
<td>62,633</td>
</tr>
<tr>
<td>Dutiable</td>
<td>73,224</td>
<td>55,232</td>
<td>Other indigenous oils</td>
<td>27,332</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Foreign oils, duty-free</td>
<td>1,815</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dutiable</td>
<td>4,800</td>
</tr>
<tr>
<td>Nov.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duty-free</td>
<td>180,190</td>
<td>189,226</td>
<td>Peppermint Oil</td>
<td>64,266</td>
</tr>
<tr>
<td>Dutiable</td>
<td>61,707</td>
<td>70,103</td>
<td>Other indigenous oils</td>
<td>21,929</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Foreign oils, duty-free</td>
<td>7,359</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dutiable</td>
<td>2,430</td>
</tr>
<tr>
<td>Dec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Duty-free</td>
<td>199,591</td>
<td>159,463</td>
<td>Peppermint Oil</td>
<td>46,014</td>
</tr>
<tr>
<td>Dutiable</td>
<td>73,924</td>
<td>77,532</td>
<td>Other indigenous oils</td>
<td>26,627</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Foreign oils, duty-free</td>
<td>623</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>dutiable</td>
<td>2,030</td>
</tr>
</tbody>
</table>

Total value of imports in the 2nd half-year 1911 $1,429,512

" " " " " " 2nd " 1910 " 1,135,737

" " " " " " whole year 1911 $2,864,251

" " " " " " 1910 $2,446,716

Total value of exports in the 2nd half-year 1911 $485,050

" " " " " " 2nd " 1910 $405,446

" " " " " " whole year 1911 $798,484

" " " " " " 1910 $675,030

to administer proper chastisement to the bandits have failed, as the government troops are not sufficiently familiar with the country and the rebels are abetted by the rural population. Discontent is growing daily among the lower classes, and the same people who acclaimed President Madere at the time of his entry into the capital are gradually being converted into his enemies, for few of the hopes entertained of him have been fulfilled, and the President is quite unable to carry out all the promises he has made. Unfortunately an anti-foreign movement is again beginning to show itself; a very grave sign indeed, which during the Revolution led to deplorable excesses, such as the horrors of Torreon, Covadonga and other
places, some of which remain unrevenged until this day. Is it surprising, in these circumstances, that capital, nearly all of which is owned by foreigners, is very chary of investing in new undertakings in Mexico? It is earnestly to be hoped that there will be an improvement in the situation at an early date, so that the achievements of the Revolution, which has cost so much in blood and treasure, may at length be turned to the true advantage of the country.

If an inference were drawn from the good harvests of the past few seasons and from the extremely favourable sugar-prices, it would be fair to prognosticate a thoroughly satisfactory state of business in Cuba. Unfortunately this would be a false conclusion, for all hopes are disappointed by the fatal political troubles, which appear to have no end. Recent minor revolutionary risings have all been suppressed in good time, but a much more serious political conflict has now arisen. The veterans of the revolution of 1897 have made of the Government a demand which it cannot possibly grant; that is to say, the filling of all official posts by their partisans. How serious is the state of affairs may be gathered from the fact that the United States have already held out an emphatic threat of interfering for the third time — which would probably be the last. For the moment everything appears to be quiet again, but the fire continues to smoulder beneath the ashes, and is likely to break out with renewed intensity before long. Added to this there is universal dissatisfaction with the government of General Gomez.

A good idea of the economic position of Brazil (a country which takes the first rank among the South American markets for our manufactures, especially as regards artificial odoriferous substances), may be gathered from the annual report of the Deutsche Ueberseeische Bank. It is there stated that the Northern parts of the Republic, which are largely dependent upon the export of rubber, have suffered so severely from the fall in rubber-prices that the Government has been compelled to have recourse to exceptional measures (such as the abolition of customs duties on all tools and materials used in the collection and cultivation of rubber), for relieving the at times critical situation of those who are connected with the rubber-trade and industry. On the other hand those parts of the country which are interested in coffee-growing, especially the State of São Paulo, have been brilliantly prosperous. Hence the falling-off in the rubberexports has been counterbalanced by the increased value of the coffee-shipments and it is therefore probable that the commercial balance of Brazil will show a considerable excess of exports over imports for the year 1911. The statistical returns for the first 9 months of the year 1911, compared with the same period of 1910, show the following result:—

<table>
<thead>
<tr>
<th></th>
<th>Exports</th>
<th>Imports</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st January to 30th September 1911</td>
<td>£ 43,531,157</td>
<td>£ 38,662,620</td>
</tr>
<tr>
<td>1st &quot; 30th &quot; 1910</td>
<td>£ 44,567,555</td>
<td>£ 34,088,068</td>
</tr>
</tbody>
</table>

2*
This excess in value of exports, in conjunction with the uninterrupted influx of foreign capital in the form of State-loans, Federal-loans and City-loans, the acquisition of mortgages, shares and debentures in Brazilian undertakings, and the supply of materials for public and private buildings and for railways, has kept the rate of exchange for 90 days' acceptances on London at over 16 d. almost throughout the year, and has kept the fluctuations down to a very limited range, between 16 d. and 16\(\frac{1}{4}\) d., whereas in the year 1910 the Brazilian rate of exchange fluctuated from 15\(\frac{1}{16}\) d. to 18\(\frac{1}{4}\) d.

The Brazilian Government is continuing its broadly-planned policy of opening-up the country. It has further extended its railway-system and has taken in hand a series of new and important lines in several States, including Bahia, Ceará, Santa Catharina and Paraná. The energy displayed by the Government in rapidly increasing the means of communication and in carrying out new harbour-works and public-health undertakings on the widest scale throughout the vast extent of the Republic brings with it as a matter of course an urgent need of capital, and leads to a succession of fresh loans in the country itself and abroad.

In the neighbouring Republic of Uruguay trade has expanded in a satisfactory manner, and under its new President the social development of the country has taken a long step forward. As it is fair to assume that the new Government will continue to display a sound understanding of the economic needs of the country the continuance of favourable prospects may be looked for, always presuming that these bright hopes are not again brought to naught by a failure of the harvest. The following figures indicate the growth of imports and exports in the course of the past year:

<table>
<thead>
<tr>
<th>Year</th>
<th>Exports</th>
<th>Imports</th>
</tr>
</thead>
<tbody>
<tr>
<td>1911</td>
<td>$44,536,000</td>
<td>$43,481,000</td>
</tr>
<tr>
<td>1910</td>
<td>$43,700,000</td>
<td>$41,151,000</td>
</tr>
</tbody>
</table>

The sale of our manufactures in Argentina continues to present a cheerful picture. The commercial situation of the country has further improved during the winter, if not strikingly, at any rate in a degree commensurate with the favourable crop prospects. The area under crops has been considerably extended, and the maize-crop in particular promises to yield a splendid return, judging by the estimates at present available. According to a report published by the Argentine Department of Agriculture, the total value of the crop of cereals and linseed is computed as follows:

<table>
<thead>
<tr>
<th>Crops</th>
<th>1910/11 Pesos Gold</th>
<th>1911/12 Pesos Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat</td>
<td>140,000,000</td>
<td>174,000,000</td>
</tr>
<tr>
<td>Linseed</td>
<td>49,000,000</td>
<td>51,000,000</td>
</tr>
<tr>
<td>Oats</td>
<td>15,000,000</td>
<td>25,000,000</td>
</tr>
<tr>
<td>Maize</td>
<td>22,000,000</td>
<td>150,000,000</td>
</tr>
<tr>
<td>Total</td>
<td>226,000,000</td>
<td>400,000,000</td>
</tr>
</tbody>
</table>

This means a surplus of 174,000,000 Pesos as compared with last year.
The fact must be taken into consideration that the stocks of all imported articles are still very heavy and it is probable, therefore, that the actual revival of the export-trade to the Argentine will remain in abeyance for some little time. The difficulty with Italy appears to have been removed, for since the Argentine Congress has decided to abrogate the special sanitary measures against Italian vessels, the abolition of the Italian decree against emigration to Argentina, if not already actually carried out, may be expected in the near future. According to a communication by the German Consulate-General at Buenos Ayres, dated 13th January 1912, the total value of Argentine industrial products in the year 1911 exceeded 4000 million Marks. This increasing national production is a factor which can no longer be left out of account in considering the general economic balance of the country, and which will probably result in the commercial balance of Argentina showing for the year 1911 an excess of exports over imports. "Taking everything into consideration", the report concludes, "the country looks forward with confidence to the year 1912".

The conditions of export-business to Chili have been quite favourable in 1911, for the activity in the nitrate of soda trade has infused new vigour into the country. The official returns of foreign trade show an increase both in imports and exports, but here, too, there are indications pointing to the beginning of an accumulation of imported merchandise. In the year 1911 the imports have for the first time exceeded the exports, the balance representing a value of nearly $10,000,000. The crop-prospects are said to be favourable, whereas it is known that last year's harvest, owing to drought, was not a good one. Still, after a series of favourable harvests such as has occurred in Chili, this single failure of crops does not signify very much. The condition of the national finances, however, remains unfavourable. Internal and external debt, paper money and railway-guarantees have, it is said, piled up a National Debt of 1000 million Pesos paper, representing over 300 Pesos paper per head of the population, a figure equalled in no other country. It is to be desired that ways and means will be found to take up with some energy the paying-off of foreign loans, for this is the only way of putting an end to the instability of the rate of exchange, which is such a serious obstacle to the economic progress of Chili.

It is to be regretted that in Peru no change for the better can be discerned. It is true that agriculture continues to develop favourably and that cotton, sugar and rice have realized profitable prices, but the greater part of the natural wealth of the country is still awaiting rational exploitation. We understand that much is expected for Peru from the opening of the Panamá Canal, and that it is believed that, when this has been accomplished, North American enterprise will turn towards the country. It is to be hoped that these dreams may be realized, but we doubt whether, for some years to come, much can be expected from the purchasing
power of this market, where at present the consumption of articles of our branch of industry is very moderate.

Japan has once more been favoured by excellent rice- and silk-crops, and experience shows that a satisfactory consequence of such a result is an increased demand for articles of luxury by all classes of the population. Business in our branch, which, owing to the necessity of the people to practise economy, as explained in our last October Report, had been quiet throughout the first half of the year, was just beginning to revive in the autumn when suddenly the outbreak of the revolution in China put an end to all hopes. As a large proportion of our goods is worked up in Japan for subsequent export to China, it is not surprising that the state of insecurity of the latter country, which is such an important selling-market for Japanese products, at once brought about a restriction of business with the former. The demand for the Japanese home-trade has been satisfactory. High expectations are entertained in Japan of the Sayonji-Ministry, which has now been in power for some months and is apparently imbued with an earnest desire to place the finances of the country upon a more healthy footing. Similar endeavours by the Katsura Government were failures. The Marquis Katsura himself, as an old soldier, was unable or unwilling to place some curb upon his eagerness for a further increase in the Navy and the Army, and his financial reform-schemes were therefore doomed to failure. In the Budget recently brought in by the Minister of Finance, Yamamoto, the new credits for the fighting services have been restricted to a minimum. If the new Government should be long-lived, there is ground for hoping that there will be a thoroughgoing improvement in the national finances, with a consequent increase in the purchasing power of the people.

Of the foreign trade of Japan in the year 1911 the Deutsche Export-Revue gives the following particulars: “The total value of the external trade of Japan in the past year exceeded 1018 million yen, being made up as follows (in 1000 yen): Exports 488602 (against 472552 in 1910), imports 529222 (against 472347 in 1910); to which must be added bullion exports 29349 (25521) and imports 24385 (22659). Although the figures for 1911 constitute a record, the Japanese export returns were nevertheless not quite satisfactory, as the great expectations that were entertained at the beginning of the year did not come to fruition. This was due in the first place to the outbreak of the Chinese revolution, which lamed trade with that country for the time being. The imports showed a considerable increase, partly the result of the coming into force of the new Customs Tariff in July of last year, and partly owing to the considerable importation of rice consequent upon the failure of the previous year’s (1910) rice-crop in Japan.”

As regards China, we have but little to report, and that little is unsatisfactory. The heavy wounds inflicted upon all parts of the country
by the revolution are only too familiar ground, and it need scarcely be
stated that while everything is at sixes and sevens all business-intercourse
with this great market is suffering heavily. A considerable time must
elapse before the new form of Government can inspire confidence, and
before a return of peace and security will permit of the revival of trade
and traffic from their present prostrate condition.

Commercial Notes and Scientific Information
on Essential Oils.

Oil of Acronychia laurifolia, Bl. At Buitenzorg1) 198 kilos leaves
of this laurel, known in Java as kisarira, yielded 133 cc. oil, possessing
the following constants: \( d_{20} 0,915 \), \( a_D +1^\circ 52' \), sap. v. 11, ester v. after
acet. 50,9. The oil contained no aldehydes.

Almond Oil, pressed, from Almonds (German Pharmacopoeia V). The hope of lower prices which we expressed in our last Report has un-
fortunately not been fulfilled, for throughout the winter months the ap-
pearance of both the Apulian and the Sicilian almond markets has been
very firm indeed. In spite of the high prices the product of last year's
crop found ready buyers, and at present only small stocks are left, for
which 208 \( \text{\textcurrency} \) per 100 kilos is asked. The available reports with regard
to the present state of the flowers are favourable, but the danger of frost
will not be past until after the next four weeks, and it would therefore
be premature at this stage to describe the coming crop as in all pro-
bability likely to be a good one. The prices of almonds of the new crop
for future delivery, which are at present entirely speculative, have fallen
by a few marks as a result of the prospects. During the winter the sale
of our own expressed almond oil has been normal, and there was no
difficulty in obtaining the unaltered high prices. As already stated the
remaining stocks of sweet almonds are small, and doubtless therefore the
present value will be maintained until the summer.

Almond Oil, pressed, from Apricot kernels. The forecast in our
last Report of the probable course of the apricot-kernel market has on
the whole been fulfilled. The deficiency in the Californian crop prevented
a further fall in prices, which otherwise would probably have followed
upon the favourable crop in the district of Damascus, and the quotations,
with few fluctuations, remained at about 69 \( \text{\textcurrency} \) per 100 kilos. After the
outbreak of the war between Italy and Turkey some depression had been

1) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49.
expected, Italy being an important consuming market of apricot kernels, and commercial intercourse between the two countries having ceased entirely owing to the enormous war-duities imposed by the Customs of each nation upon the products of the other. But it would seem that Italy had covered her principal requirements before the outbreak of the war. In Hamburg the demand has left somewhat to be desired; in that market attention has been paid to Japanese and Chinese kernels, which were obtainable more cheaply than Damascene kernels, at any rate temporarily. It will be remembered that we had already revised our prices for expressed almond oil from apricot kernels in the previous autumn, in order to bring them into accord with the new market value of the 1911 crop; hence our quotations could remain unaltered. The demand has been normal, and so has that for genuine essential bitter-almond oil, although, since the incorporation into the Pharmacopeias of artificial chlorine-free bitter almond oil, and the consequent admission of that product in the manufacture of articles for human consumption, the cheaper artificial oil is of course preferred in many quarters. There is, however, a not unimportant difference between the two oils in respect of taste, and this is often disregarded by the manufacturers who employ these oils. It may be added, however, that manufacturers who have formerly been in the habit of using "very cheap" bitter almond oils, free from hydrocyanic acid, with a "guarantee of genuineness", are obviously unlikely to notice much difference when employing artificial oil.

G. Bertrand and A. Compton), who have recently been engaged in investigations on the influence of temperature upon the activity of emulsin, have discovered that at a raised temperature the constituents of emulsin, amygdalinase and amygdalase, affect amygdalin almost equally. In the course of an experiment extending over 15 hours the maximum action of the enzymes upon amygdalin is attained at about $+40^\circ$; in a two hours' experiment at about $+56^\circ$ for amygdalase, and at about $+58^\circ$ for amygdalinase.

**Ambrette Seed Oil.** The price of ambrette seed has risen by more than 100 per cent. in the course of the last twelvemonth, and the only reason why ambrette seed oil maintained its previous cheap price for some considerable time was the existence of fairly large stocks both of seed and of oil. These have now been cleared off, and our quotations have followed the market-value. It is now a considerable time since supplies have come to hand from the various countries of production, and for the present orders for the raw material can only be placed at prices which must be described as exorbitant.

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Up to the present little is known of the properties of the valuable oil of ambrette seed, for which reason we record below, as a matter of general interest, the limits of the constants of our own distillates prepared in the course of the last few years, as determined by us. It is well-known that the normal distillate of ambrette seed is of a wax-like consistency, due to the large proportion of high-molecular fatty acids (palmitic acid) which it contains, and that the liquid oil, from which all odourless admixtures have been removed, is obtainable only by special treatment.

1. Normal, solid distillate:

\[
\begin{align*}
\text{d}_{40} & \quad \text{acid v.} \quad \text{ester v.} \quad \text{sol. pt.} \\
0.891 & \quad 75 \quad 66 \quad 38 & \text{insol. in 10 vols.} \\
0.892 & \quad 132 \quad 113 \quad 390 & 90\% \text{ alcohol.}
\end{align*}
\]

A product melting at about 47° gave \(d_{50,0}\) 0.8834 and was soluble in about twice its vol. and more 90% alcohol.

2. Liquid Oil:

\[
\begin{align*}
\text{d}_{15,0} & \quad \alpha_0 \quad n_{0,020} \quad \text{acid v.} \quad \text{ester v.} \\
0.9088 & \quad +0°14' \quad 1.47421 \quad 0 \quad 167.7 & \text{sol. in 3 to 6 vols. a.m.} \\
0.9123 & \quad +1°19' \quad 1.47646 \quad 2.4 \quad 180.5 & 80\% \text{ alcohol.}
\end{align*}
\]

Oil of Andropogon intermedius\(^1\)). This species of Andropogon (comp. Report April 1909, 18) contains, as ascertained at Buitenzorg\(^1\)), only 0.03% oil: \(d_{26,0}\) 0.919, \(\alpha_D -15°30'\). Andropogon odoratus\(^2\)) yielded 0.35% oil (\(d_{26,0}\) 0.914; \(\alpha_D -31°10'\)), while the distillation of Andropogon procerus\(^2\)) only afforded 0.08% oil.

Angelica Oils. The scanty quantity of oil produced as the result of last autumn's distilling-season has of course maintained its exceptionally high level of prices throughout the winter, and it was only the approaching spring which induced several manufacturers somewhat to moderate their demands. We have followed this decline in our own quotations. In our opinion there is no cause for anticipating that the result of the present year's crop will be specially favourable, seeing that young plants are wanting everywhere, the 1911 sowings, both here at Miltitz and in Thuringia, having been a total failure owing to drought. It is therefore probable that the market conditions will shape themselves practically the same as last year, and consumers will be well-advised if they cover their requirements for the present year at the prices now current, which are in our view only transitory. The unfavourable conditions prevailing in angelica

\(^1\)\) The author-names are not stated in the original; we suppose that Andropogon intermedius, R. Br. and A. odoratus, Lisb. are meant. The latter was referred to in our Report of April 1907, p. 36.

\(^2\)\) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 48, 49.
root oil also apply to angelica seed oil. Our moderate stocks have been exhausted and for the present, therefore, we are compelled to refuse orders of importance, such as come to hand from time to time, especially from England. We only expect a small yield next autumn from our own plantations, but possibly, before that time, we may by chance discover elsewhere a parcel of raw material for distilling.

Anise Oil, Russian. Already in our last Report we pointed out that the yield of the 1911-crop had fallen far below that of the previous year, and the advices which have since come to hand have unfortunately not only confirmed our statement, but have placed the fact of the complete failure of the crop beyond doubt. In well-informed quarters the total quantity harvested is estimated to have been 100000 Poods, as compared with 245000 Poods in the year 1910. At the close of the last fair at Alexeyewka, which, owing to the delayed supplies, could not be held until November 14, it was possible to obtain a general idea of the paucity of the yield. Qualitatively also, the anise brought to market was worse than had been expected, and for seed with a very poor oil-yield from 53 to 55 per 100 kilos cif. Hamburg was asked. In these circumstances it is hardly necessary to say that the distillers of anise in Russia were only able to manufacture sufficient for their barest necessities, especially because, with such prices as these for their raw material, it was impossible for them to compete successfully with pure anethol, in the manufacture of which, fortunately, anise seed can be dispensed with. The prices of pure Russian anise oil with high solidifying point (18°) at times approached as high a figure as 20, but this quotation could not be long maintained in view of the reserved attitude of the buyers. At the moment it would be possible to buy from first hand at about 17,75 to 18, but in spite of this the market must be called exceedingly firm.

Apopin Oil, see Linaloe Oil, p. 92.

Arnica Oils. We have at our disposal a sufficiency of the finest arnica flower oil of our own distillation to last us until the summer; on the other hand there is still a complete lack of arnica root oil (an article which is in fairly strong demand in the cosmetics trade), because in spite of all our efforts we have been unable to discover any raw material for distilling purposes. The reports from all districts where arnica root is gathered agree in stating that no supplies of any sort have come to hand, owing to the exceptional drought of last summer.

Oil of Artemisia frigida, Willd. ("Wild Sage"). The oil of this American Composita, which was described by Rabak 1) some years ago has since then been more closely examined by him 2). The plant, which was

1) Comp. Report October 1906, 12; April 1907, 13.
collected in South Dakota, yielded 0.26% oil (calc. based upon green herb?), possessing the following constants: $d_{25}^0$ 0.940, $\alpha_{D}^0 = 24.2^\circ$, $n_{D25}^0$ 1.4716, sol. in 1 vol. 80% alcohol, acid v. 2.5, ester v. 25, ester v. after acet. 139. When the oil was allowed to stand 3% l-borneol (m. p. 203°; $[\alpha]_D^0 = 32^\circ$) separated out from it. Caprylic and cenanthic acids were probably present in the free state, and cenanthic acid, valeric acid, with traces of formic and undecylic acids, in the esterified form. The oil further contained the following constituents: 18 to 20% cineole (m. p. of the iodol-compound 110 to 113°) and 8 to 10% l-fenchone (m. p. of the oxime 164 to 165°). The oil contains a total of 43% borneol, of which 35.6% is free borneol and 6.8% is in the form of cenanthic ester.

**Oil of Artemisia lavandulæfolia (?).** A few years ago\(^1\), we referred under the name of *Artemisia lavandulæfolia* to a product distilled at Buitenzorg, which contained an unidentified solid body, possessing the molecular structure $C_{12}H_{14}O_{2}$. From a subsequent reference to this oil\(^2\), we gather that it is most probably derived from another plant than that named above, but so far it had been impossible to procure a fresh supply of raw material to elucidate the botanical origin. The solid body is precipitated in the oil when light petroleum is added. It has m. p. 32.5 to 33°, contains a methoxyl-group and absorbs 3 molecules bromine. The body was heated for a few hours with potash liquor, consuming 2 molecules potassium hydroxide. The reaction-product was then treated with steam, when a body with an odour of amyacetate passed over. This was possibly methyl heptenone. With iodine and potash liquor the distillate gave a pronounced iodoform reaction. After acidulation, n-butyric acid distilled over. The solid body probably represents the methylester of an unstable acid.

**Asafoetida Oil.** In a paper on the detection of galbanum and ammoniacum in asafoetida, H. M. Sechler and M. Becker\(^3\) state, *inter alia*, that such an admixture is also observable in the essential oil obtained from the resin in question. While pure asafoetida is said to yield a colourless oil\(^4\), asafoetida adulterated with galbanum or ammoniacum yields a more or less yellow-coloured distillate. It is stated that an addition to asafoetida of as little as 10% of the gum-resins referred to may be detected by this test.

It is further asserted that the refractive index also affords a guide to the possible adulteration of asafoetida with galbanum or ammoniacum, the refraction of the last-named resins being lower than that of asafoetida. Sechler and Becker regard an asafoetida oil with a coefficient of refraction

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\(^1\) Report April 1909, 20.

\(^2\) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 45.

\(^3\) Americ. Journ. Pharm. 84 (1912), 4.

\(^4\) Gildemeister and Hoffmann, in *The Volatile Oils* (p. 574), stated that the colour of asafoetida oil varies from yellow to brown.
below 1,4960 (25°) as suspect, an assumption which seems to be very
much in need of corroboration, and which, for instance, is not in accord
with the statements by E. F. Harrison and P. A. W. Self set forth below.

Harrison and Self\(^1\) have also investigated asafætida and have pre-
presented the results of their observations in a paper read before the Phar-
aceutical Society of Great Britain. They examined 15 different samples of
asafætida, drawn from large parcels. They determined the percentages
of loss on drying in a water-oven, the percentage of resin, of mineral
constituents (ash) and of essential oil. The latter they examined more
closely. With the exception of one sample, which came from Bombay,
all the samples had been taken from parcels imported from the Persian
Gulf. We will here only refer to that part of the interesting paper which
deals with the examination of the essential oil.

Harrison and Self determined the oil-content of each sample by steam-
distillation. By this method they obtained from 5,8 to 17,1\(^{\circ}\) oil, that is
to say, in part considerably higher yields than had been observed pre-
viously\(^2\). Umney and Bunker\(^3\) alone have obtained approximately equal
values (from 12 to 16\(^{\circ}\)) but these were obtained by a different method
of determination.

The characters of the oils obtained from Persian asafætida fell within
the following limits of value: \(d_{15.50}\) 0,915 to 0,981, \(\alpha_d + 9^{\circ} 39^{\prime}\) to \(-17^{\circ} 3^{\prime}\),
\(n_{D20}\) 1,4942 to 1,5207. Sulphur-content 17,5 to 29,2\(^{\circ}\). A high sulphur-
content was mostly found in combination with high sp. gr., high refraction,
and dextrorotation.

The gum-resin from Bombay yielded 7,5\(^{\circ}\) oil of somewhat different
constants \(d_{15.50} 0,993; \alpha_d - 35^{\circ} 55^{\prime}; n_{D20} 1,5250; 37,8\(^{\circ}\) sulphur\) and, ac-
cording to Harrison and Self, is probably less valuable than the other
samples.

The experience of Umney and Bunker (\textit{loc. cit.}) that oil from asafætida
in tears contains a higher proportion of sulphur than oil from asafætida
in mass has not been confirmed by Harrison and Self; on the contrary,
their samples showed the same average sulphur-content, whether mass or
tears. They believe that Umney and Bunker have operated under serious
loss of sulphur, volatile sulphur-compounds having escaped in the course
of their examination. They themselves have tried to determine the sulphur-
content by different methods and have come to the conclusion that the
following method is that which yields the best results:

About 0,5 g. of the oil is weighed into a 150 cc. flask, connected by
a ground joint to the tube of a vertical condenser; 5 cc. of water is added
through the tube, followed by 5 cc. of nitric acid \(d_{15.50} 1,42\). The flask

\(^1\) Pharmaceutical Journ. 88 (1912), 205.
\(^2\) Gildemeister and Hoffmann (\textit{loc. cit.}) give from 3 to 6,7\(^{\circ}\)
\(^3\) Comp. Report October 1910, 20.
is warmed, if necessary to start the action, which then proceeds somewhat vigorously. Next 3 g. of powdered potassium bromide is dropped in through the condenser tube, the liquid boiled for ten minutes, cooled, and 5 g. of caustic soda, dissolved in a little water, added in the same manner. The liquid is then evaporated to dryness in a platinum vessel and ignited. The residue is dissolved in water, nitric and nitrous acid removed by evaporation with hydrochloric acid, and the sulphate determined in the usual way.

According to Harrison and Self the best evidence of the value of asofoetida is to calculate the sulphur-content of the oil for the drug after deducting the ash. Present experience shows that the oil of the genuine drug does not contain less than 1,5% of sulphur.

Oil of Sweet Basil. This article continues to suffer from lack of enquiry, and as a result there has been some accumulation of stock. Offers of considerable quantities from some of the producing centres appear to show that the distillation of the oil has again been taken up somewhat more assiduously than formely. We must, however, earnestly caution the producers against indulging in too optimistic anticipations of the future of this article, for its consumption has decidedly decreased, and even at a heavy sacrifice it would be very difficult to dispose of large quantities.

Bay Oil. The scarcity which we have had to chronicle for several years past still continues, and the small arrivals which have come to hand from time to time at Havre, Marseilles and Hamburg have always found ready takers. Occasionally the supplies consisted of oil which had been adulterated almost out of recognition, and scarcely deserved the name of bay oil. Judging by the most recent advices the present conditions of the market are likely to continue for some considerable time, inasmuch as the native producers in the West Indian Islands have again begun to complain that it is difficult to procure sufficient quantities of leaves. In any case there is not the slightest prospect of our being able to resume distilling operations here, which we regret the more because none of the parcels of West Indian oil which have thus far come into our possession even distantly approaches in quality our own distillate. We must limit ourselves to the exercise of the greatest possible care in selection from among the supplies of oil which come to market, but in doing so we are not always able to satisfy all our customers' requirements in the matter of prices, for it goes without saying that we ourselves have to pay proportionately high rates for the finer qualities. In spite of the considerable increase in price which we have been compelled to make, our exquisite terpeneless bay oil continues to be in strong demand, which proves that the high value of this product is justified by its excellence.
Bayberry Oil. An oil distilled by F. Rabak 1) from the leaves and twigs of Myrica cerifera, L. (N. O. Myricaceae) gave the following constants: d 0,9168, [α]_D = 1,5°, n_Д50 1,4945, acid v. 3,5, ester v. 21, sap. v. after acet. 58. The oil was soluble in one-half its own vol. of 90%/ alcohol, the solution becoming turbid upon the addition of 2 vols. or more; it was insoluble in 80%/ alcohol. The yield was 0,015%/ (calc. based upon green herb?).

Rabak describes the oil as a novelty, but this is not quite correct, the distillate having been mentioned by Hambrecht 2) as long ago as the year 1863, and having been described by us in our Report of October 1894, p. 70.

Birch Bud Oil. A few weeks ago we were successful in procuring in Russia a fine parcel of birch buds, the distillation of which has enabled us to make a corresponding reduction in our prices. We strongly urge the larger consumers to secure a quantity for delivery as required, experience having shown that it is very often difficult to procure supplies of raw material.

Buchu Leaf Oil. Unfortunately there has been no change in the position of this article. We have not yet succeeded in replenishing our stocks, for we have been unable to discover raw material suitable for distilling. The demand, it is true, has been very slight, so that the lack of supplies has not been particularly severely felt.

Oil of Bupleurum fruticosum. L. Francesconi and G. Sanna 3) have discovered that the oil of this umbellifer 4), in addition to an alcohol and an ether of unknown character, contains a large proportion of a terpene possessing the following characters: b. p. 167 to 169°, d_140 0,8416, α_Д50 + 35,7°, n 1,4862. It polymerises into a white, amorphous mass, m. p. 90 to 100° ([α]_D = 66,14°).

The same authors, in another paper, which has been published in the Atti R. Accad. dei Lincei, Roma (5), 20, II. (1911), p. 190 5), describe the action of nitrosyl chloride upon the essential oil. They dissolved 5 cc. of the oil in 20 cc. alcohol, admixed thereto 7 cc. amyl nitrite or 11 cc. ethyl nitrite and diluted with 8,5 to 9 cc. alcohol which had been saturated with hydrogen chloride. Treated by this method, the various fractions always yielded the same nitrosochloride, whereas Wallach’s method gave no result. The nitrosochloride probably represents a mixture; it melts between 80 and 97°, chiefly between 92 and 94°; [α]_D = 196,2 to −210,6°. By dissolving

1) Midland Drugg. and pharm. Review 45 (1911), 484.
3) Gazz. chim. ital. 41 (1911), l. 796. Copies of this paper, and of those mentioned in the succeeding paragraphs, were kindly sent to us by the authors. Quoted from Chem. Zentralbl. 1911, II. 1450.
4) Comp. Report October 1911, 23.
5) Quoted from Chem. Zentralbl. 1911, II. 1805.
in chloroform and precipitating with methyl alcohol it can be split up into a less soluble portion, m. p. 100 to 101° ([α]_D — 285°), and a more readily soluble portion, m. p. 101 to 102° ([α]_D — 175°). From the nitrosochloride Francesconi and Sernagiotto 1) obtained dihydrocuminic aldehyde.

By eliminating nitrosylchloride from the nitrosochloride the authors obtained d-β-phellandrene ([α]_D + 19,65 to 53,32°). Whether the oil also contains α-phellandrene is very doubtful. The authors 2) prepared the dihydrocuminic aldehyde by prolonged boiling of the nitrosochloride with a mixture of 3 parts water and 10 parts acetic acid. Its characters are as follows: b. p. 136 to 140° (15 mm.), d_{190} 0,9825, n 1,528. The semicarbazone melts between 197 and 198°. When oxidised with oxide of silver in alcoholic solution it forms cuminic acid (m. p. 116 to 117°).

From the phyto-physiological standpoint, the investigations of Francesconi and Sernagiotto 3) into the localisation and distribution of the essential oil in the Bupleurum plant are also interesting. The younger the leaves, the greater their essential-oil content. The presence of oil may be detected not only by extraction but also microscopically by means of osmic acid, "Soudan III" (aminoazobenzolazo-β-naphthol) or Mesnard’s reagent.

The authors 4) give the following particulars of the oil-yield: the branches of plants distilled at Laconi (prov. of Cagliari) contained 1°/0 oil; the leaves, during the flowering period, yielded from 1 to 3°/0, and the flowers distilled separately, 3,75°/0 oil. The calculation of the yields appears to be based upon the green herb.

**Cajuput Oil.** Business in this article has taken a somewhat more animated turn within the past six months, and as a result the export figures up to the end of November, which are the latest available, show an advance as compared with those of the corresponding period of last year. The shipments were as follows:

<table>
<thead>
<tr>
<th>Year</th>
<th>Baskets</th>
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<tr>
<td>1911</td>
<td>1862</td>
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<td>1910</td>
<td>1536</td>
</tr>
<tr>
<td>1909</td>
<td>1309</td>
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As mentioned in our last Report, the total exports for the year 1910 amounted to 1739 baskets, that is to say considerably less than the shipments of the first eleven months of 1911.


We have again received, quite lately, considerable parcels of this oil from our reliable source of supply in the island of Buru, and these are not included in the figures given above.

The prices have been subject to slight fluctuations only and, generally speaking, have maintained their present level.

**Calamus Oil.** In directing attention to our superior distillate, we do so with the more emphasis because just lately we have been asked to give an opinion on oil-samples from competing quarters which, although normal as regards their constants, possessed such a peculiar aroma that their employment in, say, the manufacture of liqueurs, must be attended with serious and costly disappointments. For this reason we would earnestly point out to those who are interested in the article, and especially to the distributors, that in purchasing calamus oil it is quite a mistake to regard the question of price as of prime importance.

**Camphor Oil.** On the whole the position of this important oil may be described as unaltered. Considerable stocks of cheap crude oil still exist both in Europe and in the United States, and for that reason the selling prices have not as yet reflected the increased rates which have had to be paid to the Japanese for the most recent purchases. Both light and heavy camphor oil have been in brisk demand; considerable quantities have changed hands, and the weakness in the turpentine oil market has by no means been able to hamper the trade in camphor oil. Generally speaking the position of the article must be called very firm, for the Japanese refuse altogether even to consider counter-offers to their demands, and they are very cleverly taking care to place upon the market only just enough of the different varieties of crude oil to supply the demand for the time being, and above all to prevent an over-supply.

In our Report of April 1911, p. 31, we stated that a Mr. Anderson, an American interested in the camphor trade, had lodged a protest with the Japanese authorities against certain alleged irregularities practised in that trade. In view of the antagonistic interests of the Japanese and the foreign camphor-refiners, Mr. Anderson has come to the conclusion that the only means of saving the camphor trade is the creation of a Trust, embracing the Japanese and the American manufacturers, and also, if possible, the British, German, and French importers. He has explained his views to the leading interests in Japan and in the United States, but it is considered doubtful whether it will be possible to secure the cooperation of the parties in Europe who are interested in the trade, although there may be no difficulty in bringing "under one hat" the Japanese and the American manufacturers. It is said that the Japanese firms have

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made it a condition that the Trust shall buy from them 12,000,000 lbs. of camphor annually.

According to a British Consular Report¹ the Japanese camphor refiners, at the beginning of last year, complained to their Government of being compelled to pay 5.80 yen per 100 kin more their camphor than was charged to their competitors in Europe and America, whereupon the Monopoly Bureau raised the price of the "BB" brand of camphor from £ 7.5/- to £ 7.10/-. The total production of camphor in Japan in the year 1910 remained below the estimated figure of 770,000 lbs.; the experiments for preparing camphor from the leaves are as yet (still?) in the initial stage. The forests in Southern Formosa, which have been principally exploited up to the present, yield a product which often contains 400 parts of oil to 100 parts of camphor, while the product of the Northern forests, which have recently been secured by force of arms from the attacks of the aborigines, only yields 75 parts of oil to 100 parts of camphor. For this reason it is probable that the year 1911 will already show a considerable increase in the camphor-production of Formosa.

From the XIth Financial and Economic Year-Book for Japan we quote (through a trade report) the following particulars concerning the production and export of camphor in Japan and Formosa²).

In Old Japan the output of crude camphor from 1931 distilling-plants amounted to 135,4454 kin, representing a value of 798,489 yen. The exports in the year 1910 (whether of crude camphor only or of crude camphor and camphor refined in Japan is not clear), represented the following values:

<table>
<thead>
<tr>
<th>Destination</th>
<th>Amount (Yen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>To British India</td>
<td>477,649</td>
</tr>
<tr>
<td>&quot; France</td>
<td>748,626</td>
</tr>
<tr>
<td>&quot; Germany</td>
<td>322,430</td>
</tr>
<tr>
<td>&quot; United Kingdom</td>
<td>580,023</td>
</tr>
<tr>
<td>&quot; U. S. A.</td>
<td>691,029</td>
</tr>
<tr>
<td>&quot; Other countries</td>
<td>144,612</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2,964,369</strong></td>
</tr>
</tbody>
</table>

In connection with the above it should be stated that the great fluctuations in the exports to France, Germany and the United Kingdom are explained by the fact that the individual cargoes are usually shipped under option London, Havre, or Hamburg, and that in every case the first port touched by the steamer carrying the freight is regarded as the place of export for statistical purposes.

The production of camphor in Formosa has remained fairly stable in recent years, whereas the value of the exports shows considerable fluctuations:

²) Comp. our previous communications, Report April 1911, 32 e. s.
According to B. A. Bond it is estimated that the camphor forests of Formosa will be exhausted in 45 years' time, but since 1901 the Japanese Government has caused 15000000 young trees to be planted.

According to a U. S. A. Consular Report\(^2\) from Tamsui in Formosa, the camphor exports from that island during the first eleven months of the year 1911 amounted to 4788270 lbs., value $1486934. This represents a decline in value of $100000 in round figures as compared with the corresponding period of the previous year. This reduction is chiefly accounted for by a falling-off in the exports to the U. S. A., but the shipments to Germany and France are also said to have declined. According to a report received at the Bureau of Labour of the U. S.\(^3\) a similar reduction is shown in the export-figures relating to Chinese camphor from the port of Foochow, which fell from 524800 lbs. in the year 1909 to 130800 lbs. in the year 1910. The principal refinery, which was carried on by a British firm, has closed down, and only one refinery still keeps going. Crude camphor is scarce, and from the forests in the interior no increased supplies are to be expected.

In our Report of April 1911 we called attention (p. 36) to the decrease which was taking place in the exports of camphor from China. We give below the statistics of the exports from the ports of Shanghai, Amoy, and Foochow, taken from a French journal\(^4\): —

<table>
<thead>
<tr>
<th>Production</th>
<th>Value of Exports</th>
</tr>
</thead>
<tbody>
<tr>
<td>1907</td>
<td>3914598 Kin</td>
</tr>
<tr>
<td>1908</td>
<td>3534970 &quot;</td>
</tr>
<tr>
<td>1909</td>
<td>3537712 &quot;</td>
</tr>
<tr>
<td>1910</td>
<td>4864704 &quot;(^1)</td>
</tr>
</tbody>
</table>

According to our Report of 1911 we called attention (p. 36) to the decrease which was taking place in the exports of camphor from China. We give below the statistics of the exports from the ports of Shanghai, Amoy, and Foochow, taken from a French journal\(^4\): —

<table>
<thead>
<tr>
<th>Export in Piculs</th>
<th>1907</th>
<th>1908</th>
<th>1909</th>
<th>1910</th>
</tr>
</thead>
<tbody>
<tr>
<td>Via Shanghai</td>
<td>4 607</td>
<td>4 064</td>
<td>4 889</td>
<td>4 410</td>
</tr>
<tr>
<td>Via Amoy and Foochow</td>
<td>19 711</td>
<td>8 257</td>
<td>3 945</td>
<td>1 005</td>
</tr>
</tbody>
</table>

In our last Report (p. 27) we referred to a statement by Hutchins on the occurrence of camphor-trees in German East Africa. Hutchins declared in his article that neither the botanists of the Imperial German Biological-Agricultural Institute at Amani, nor the forest officials at Wilhelmstal had recognised the tree. This statement, we are informed by Prof. Zimmerman, Director of the Institute in question, is incorrect; on the contrary, the tree was perfectly well known to the officials at Amani by the name of Ocotea

\(^1\) Comp. Report October 1911, 25.

\(^2\) Oil, Paint and Drug Reporter 81 (1911), No. 1, p. 28 F.

\(^3\) Ibidem, p. 40.

\(^4\) Journ. d'Agriculture tropicale 11 (1911), 319.
usambarensis, Engl. An oil prepared from its bark at Amani was examined and described many years ago by Schmidt and Weilinger\(^1\). The bark has also been tested for tanning-materials, but it is said to contain only about 11\(^\circ\) of the latter\(^2\).

It is only now made known by a lengthy quotation in the Bulletin of the Imperial Institute [Vol. 9 (1911), 340] from a Report on the Forests of British East Africa, 1909, that Hutchins himself as long ago as 1909 had identified the tree which he describes as "Ibean Camphor tree", as Ocotea usambarensis, Engl. Nothing of this kind was stated in the abstract which served as the basis for the paragraph in our Report of October 1911.

Schmidt and Weilinger at the time only examined the oil from the bark of the tree, but the Imperial Institute had at its disposal a series of samples of the wood in the shape of sap-wood possessing a faint odour of eucalyptus oil; branches and twigs, which, when newly broken, also gave off the same odour, but in a more marked degree; and, lastly, pollard shoots which had sprung up from the stumps of felled trees after a few years' interval. Each of these three samples, when distilled with steam, yielded a volatile oil possessing the following properties:

<table>
<thead>
<tr>
<th></th>
<th>Sapwood</th>
<th>Branches and twigs</th>
<th>Branches and twigs (Pollard shoots)</th>
<th>Bark; Schmidt and Weilinger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield</td>
<td>0,4(^\circ)</td>
<td>0,52(^\circ)</td>
<td>0,14(^\circ)</td>
<td>0,15(^\circ)</td>
</tr>
<tr>
<td>(d_{150})</td>
<td>0,9641</td>
<td>0,9681</td>
<td>0,9327</td>
<td>0,913 bei 20(^\circ)</td>
</tr>
<tr>
<td>(a_p)</td>
<td>-7(^\circ) 30'</td>
<td>-7(^\circ) 30'</td>
<td>-0(^\circ) 28'</td>
<td>-11(^\circ) 12'</td>
</tr>
<tr>
<td>Sap. v.</td>
<td>30,1</td>
<td>30,1</td>
<td>13,3</td>
<td>13,7</td>
</tr>
<tr>
<td>Sol. in 80(^\circ) alcohol</td>
<td>In 1,1 vols.</td>
<td>In 1,1 vols.</td>
<td>Insol. even in 10 vols.</td>
<td>—</td>
</tr>
</tbody>
</table>

The first two samples of oil were of a bright yellow colour and reminded of eucalyptus oil in their odour. They only contained comparatively little cineole, and no camphor could be detected in them. The oil from the shoots was of a thinner consistency than the other oils, but resembled them in odour and colour; its more powerful odour led to the conclusion that its cineole-content was greater, but the sample was too small to permit of a cineole-estimation.

In our Report of October 1910 (p. 27) we discussed a paper by Lommel on the preparation of camphor at Amani. A second paper by the same author\(^3\) contains some interesting data on the distillation of dried camphor.

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1) Berl. Berichte 39 (1906), 652; Report April 1906, 68.
2) Der Pflanzer, Ratgeber f. trop. Landwirtschaft 4 (1908), 222.
3) Der Pflanzer, Zeitschr. f. Land- und Forstwirtschaft in Deutsch-Ostafrika 7 (1911), 441.
leaves, of which a synopsis is given below: The author first deals with the distillation of leaves which had been spread out for drying in a small cinchona-plantation shortly before the setting-in of the rains, but which were not yet quite dry. The camphor-yield from these leaves was too small to make it worth while estimating it, and the experiment was set down as a failure. For a subsequent distilling-experiment a plantation was subjected to moderate cutting, when a quantity of dry fallen leaves was found on the ground between the rows of plants. These were first distilled and only yielded 0,06% crude camphor and 0,19% camphor oil, showing that they had lost almost the whole of their volatile constituents during the long time they had been lying on the ground drying, exposed to the alternating effects of rain and sun.

Next the green leaves were dried on previously cleaned ground under the shade of cultivated cinchona trees. In the course of about a fortnight they were dry enough to be readily stripped from the branches and, collected in sacks, they were carried to the still. This experiment gave a thoroughly satisfactory result, the yield being 1,55% crude camphor and 0,49% camphor oil. The result would certainly have been better still but that on one occasion, in the course of the distilling process, the condensing-water became heated, and a not inconsiderable quantity of camphor was thereby lost.

In view of the fact that present experience on the effects of cutting upon the growth of the trees shows it to be a pretty well established fact that it is possible to cut the trees twice a year, it is reasonable to expect a five-year old plantation to yield about 8400 lbs. of dry leaves per acre. This would be equivalent to an output per acre of about 325 lbs. of camphor and about 103 lbs. of camphor oil.

H. W. Emerson and E. R. Weidlein¹) have distilled camphor oil in Jamaica, and have confirmed the observation recently made that the leaves of the plant can be successfully employed for this purpose. From 56,940 kilos green leaves they obtained 1353,8 grams = 2,35% crude camphor and oil (1,32% camphor, 0,54% camphor oil and 0,49% water), and from 67 kilos dry leaves 1719,5 grams = 2,54% of a distillate comprising 1,57% camphor, 0,46% camphor oil and 0,51% water; 22425 grams twigs and green leaves yielded 0,58% camphor and 0,26% camphor oil, 8770 grams twigs and dried leaves contained 0,54% camphor, and 1800 grams wood, when distilled, yielded 0,61% camphor.

Besides camphor the oil contained pinene, phellandrene, cineole, dipentene, and safrol. It is not quite clear from the reference whether the safrol was detected by the authors in oil distilled from the leaves or

from the wood, nor do we find any particulars showing how the constituents were identified.

From an article by H. Morstatt\(^1\) on insect pests in camphor-trees we quote the following: "Although camphor, which occurs in all parts of the camphor-tree, is itself an efficient protective against the attacks of insects, it is powerless to protect the parent-tree from such pests. Thus, in German East Africa the camphor-tree is attacked by slugs, shield-lice, locusts, bugs, mites and certain kinds of beetles. The weevil, *Dicasticus Gerstaeckeri*, Faust is occasionally found in the tree in enormous numbers, and the capricorn-beetle, *Tragocephala pretiosa*, Hintz, an insect measuring from 8 to 10 inches in length, often inflicts serious damage upon the tree".

**Cananga Oil.** The upward movement in prices which all the producers agree in forecasting still continues by the way, but this notwithstanding, and in spite of the fact that the arrivals continue to be sufficient for the demand, the position of the article must be described as steadily firm. We have lately made special arrangements for securing a sufficient future supply, and in all probability our customers will therefore be secured against unpleasant surprises. In any case, however, we consider it very desirable that consumers should secure their requirements for some months ahead at the present prices, for we regard a reduction in values as quite out of the question, and an upward movement must sooner or later make itself felt when the present important second-hand stocks are beginning to be used up, and if the producers should somewhat restrict their shipments, a contingency which appears to be extremely probable in view of the exceptional quietness of the market during the past few months.

**"Cape" Oil.** On the Ivory Coast the name of *Cape* is given to a particular kind of leaves\(^2\) which are apparently used by the native women for perfuming their persons. Roure-Bertrand Fils have distilled the dry leaves, and obtained therefrom 0.28\(\%\) of an extremely mobile, greenish-yellow oil of an extraordinarily powerful, agreeable odour, at first reminding of patchouly. The distillate gave the following constants: \(d_1^{18} 0.977\), \(\alpha_D + 39^\circ 38'\), acid v. 0.7, sap. v. 109.2. It was soluble in its own volume of 80\(\%\) alcohol, the mixture showing a slight cloudiness when more alcohol was added.

**Caraway Oil.** Throughout the winter no change has been perceptible in the caraway market, but if anything the prices, as a result of the exceptionally heavy crop of last year, showed a certain dulness. Recently, however, the position has undergone a change, inasmuch as the severe winter is reported to have seriously damaged the plantations. The caraway-fields, it will be remembered, had already suffered from last year's great

\(^1\) Der Pflanzer, Zeitschr. f. Land- u. Forstwissenschaft in Deutsch-Ostafrika 8 (1912), 18.

\(^2\) Berichte von Roure-Bertrand Fils, October 1911, 43.
heat, and one-half of the area then newly-sown has had to be ploughed up. It is certain that this circumstance will bring about a material shortage in the production, but it must be borne in mind that there is still a considerable balance in reserve from 1911, which, unless bought up by speculators, will help to average the market. In the meantime the prices which, as is well-known, had dropped to the neighbourhood of fl. 11, have advanced to about fl. 15,50, and a few parcels of new crop seed for delivery next September have even changed hands at fl. 17,50. It is obvious that these facts cannot remain without influence upon the prices of caraway oil, but generally speaking we regard the reports as very premature and we are of opinion that there is still ample time for changes in the position. This, however, is certain, that there will be no return to the exceptionally low prices which resulted from last year's abnormally heavy crop.

The above is confirmed by the recently-published report of the Dutch Ministry of Agriculture, which states:

"The dry summer of 1911 has been very unfavorable to the caraway-plants. When the covering-crop was removed, the condition of the caraway-fields proved to be so bad that most of them were ploughed up. In all the important districts, such as Groningen, North-Holland, South-Holland, Zealand and Western North-Brabant, only a small section of the fields is under caraway. Thus, the State Instructor in Agriculture for Western North-Brabant estimates the area under caraway in his district at only from 10 to 20% of that of last year. The few caraway-areas which are in existence in Groningen at present date from last year. Moreover, the condition of the growing crop is not very satisfactory. In Groningen it is moderate to fairly good; in North-Holland, moderate on clay and fairly good on peat-soil; in South-Holland and Zealand moderate, and in North-Brabant bad."

**Cardamom Oil, Ceylon.** It has been necessary to raise the prices very materially, as all varieties of cardamoms suitable for distilling were almost unprocurable. The prospects are still very unfavourable and continued high values appear to be certain.

**Cardamom** Oil, **East African,** see p. 136.

**Oil of Casimiroa edulis.** Power and Callan¹) have obtained from the alcoholic extract of the seeds of *Casimiroa edulis,* La Llave (N. O. Rutaceae), a yield of 0,021°/o (calc. based upon dry seed) of an essential oil possessing the following constants: $d_20^0 = 0.9574, \alpha_D = 2°25'$ (in a 25 mm. tube). The bulk of the oil boiled below 130° (25 mm.).

**Cassia Oil.** The cassia oil market calls for very little remark on the present occasion. It is true that shortly after our last October Report

went to press the prices of 80—85% oil advanced to about 4/, because the political troubles in China were not without their effect upon the article, but towards the end of the year the market quieted down again; the quotations receded to about 3/10, and at that figure they have since remained with slight fluctuations. On the whole the demand for cassia oil has been very quiet in all the markets which count in the determination of the price of the article; the consumers' requirements have been normal and the supplies regular, and the balance between offers and demands has been undisturbed.

**Cassie Oil.** In the *Philippine Journ. of Sc.* 6, A. (1911), 350, Brooks states that *Acacia Farnesiana*, (L.) Willd. has been imported into the Philippines and now occurs wild throughout the Archipelago. In his opinion it would be worth while cultivating the plant for the sake of utilising its flowers.

**Cedarwood Oil.** Under the heading "East African Cedarwood Oil" we referred on p. 105 of our last Report to the occurrence in East Africa of *Juniperus procera*, Hochst., a conifer which is of industrial importance in the manufacture of lead-pencils. *Juniperus barbadensis*, L. to which we find references in two different publications 1) is closely related to the first-named species. It occurs in the pine-districts of Dominica, and also inhabits the other West Indian Islands, and the southern parts of North America. So far, no oil has been distilled from this plant. Besides the *Juniperus*-species mentioned above, *Pinus occidentalis*, S. W., and *Xanthoxylum martiniense*, Lam., occur in the pine-forests of Dominica.

On the oxidation of cedrene with ozone in acetic acid solution see p. 173.

**Oil of Cedrela.** F. Rabak 2) has distilled from the wood of *Cedrela odorata*, L. (N. O. Meliaceæ), a plant which occurs in the southern parts of North America, 0,3% of a golden-yellow essential oil with an odour of cedar. Its constants were as follow: d_{25}^o 0,947, n_{D50}^o 1,5038, acid v. 3,9, ester v. 41,5, ester v. after acet. 51; gives a cloudy solution with 6 vols. 80% alcohol.

**Celery Oil.** Following upon the complete failure of the celery-seed crop in France, to which we have already referred, it is not surprising that the prices of celery oil have undergone a proportionate advance. Our present selling-price is still comparatively low, inasmuch as it is based upon the cost of a few chance purchases we were able to secure, and at the current market-value of celery seed we should certainly have to pay higher rates for raw material. It is to be hoped that this year favourable weather will prevail and assure a normal crop of celery seed, for if this

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2) Midland Drugg. and pharm. Review 45 (1911), 486.
should not be the case it will be impossible to maintain the present price of celery oil, even if it should then be possible to procure any raw material at all for distilling.

**Chamomile Oil, German.** In the course of the winter we found an opportunity of procuring a few small parcels of raw material well-suited for distilling purposes, by which we were able to replenish our supplies so favourably that we were enabled slightly to reduce our prices. We are now in a position to quote special prices for important quantities and we shall be glad to receive enquiries where such quantities are in question.

**Chamomile Oil, Roman.** The small output of last season is practically exhausted, and those who have delayed covering their requirements until the new crop will be compelled to pay very high prices indeed, always assuming that they succeed in procuring a sufficient quantity at all. Our stocks have shrunk to within a very small compass and during the last few months we have been repeatedly obliged to advance our quotations.

**Champaca Oils.** B. T. Brooks\(^{1}\) has published an extensive paper on genuine champaca oil from yellow flowers (from *Michelia Champaca, L.*) an oil which has only lately been investigated by Bacon. The champaca trees which grow in the neighbourhood of Manila are rather smaller than the ylang-ylang trees. Their trunk has a diameter of from 8" to 20", while in the Botanical Gardens at Peradeniya in Ceylon there are specimens which measure from 3 to 6 feet in diameter. The trees are propagated from seed or from cuttings. The seed should be sown in sand to prevent it from rotting. In the year 1910 the trees flowered from the middle of June until the end of October, but this is exceptionally long, and was due to the comparative absence of rain during that period. The flowers must be worked up immediately after collection, as they contain a ferment which sets up an oxidising action, so that they turn brown in a short time and lose their pure odour. The oil\(^{2}\) which was prepared by Brooks has the following constants: \(d_{40}^{20} 0.904\) to 0.9107, \(n_{D30\text{O}} 1.4640\) to 1.4688, ester v. after acet. 199. It cannot be fractionated *in vacuo*, as it resinifies in the manipulation. Among the constituents of the oil Brooks found cineole (m. p. of the iodol compound 112 to 114\(^{\circ}\)) It may also contain \(p\)-cresol-methylether, but it was impossible to establish the presence of this body. When the oil was shaken with sodium bisulphite solution benzaldehyde was isolated (m. p. of the phenylhydrazone 149 to 151\(^{\circ}\). It is probable that another aldehyde is present in addition to benzaldehyde but no further investigation was made on this point. As regards alcohols, Brooks detected benzyl alcohol, which he identified by oxidising into benz-

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1) Philippine Journ. of Sc. 6, A. (1911), 333.
2) The author does not state how he prepared the oil.
aldehyde. As regards acids, benzoic acid was found to be present in the saponification-liquor. The benzaldehyde-content of the oil is about 6%, but it only contains 0,5% benzoic acid, and Brooks surmises that the last-named body is only formed by oxidation of the aldehyde or of the benzyl alcohol.

Champaca flowers contain a cristalline substance, for which Bacon sets up the empirical formula C₁₀H₁₂O₂. In contradistinction to Bacon’s observations, Brooks found that this substance reacts quantitatively with bisulphite solution, but that it cannot be recovered from the bisulphite-compound. This peculiarity renders it not improbable that the group CH : CH · CO is present in this body ⁵). The fact that the substance is a ketone is proved by its behaviour towards ammoniacal silver solution and magenta solution. The phenylhydrazone melts at 161°. The ketone does not react with acetanhydride, and with acetyl chloride it resinifies. When heated with an excess of alcoholic potash solution it gives rise to neutral succinate of potassium. It would seem that the succinic acid occurs in the ketone-molecule in the form of a neutral ester. In order to identify the alcohols which were associated with the succinic acid, the ketone was saponified with aqueous soda liquor, but only ethyl alcohol could be detected. Experiments at saponifying the body with soda liquor or with dilute acids were unsuccessful. It follows that one of the carboxyl-groups of the succinic acid is esterified with ethyl alcohol and the other with an alcohol C₁₀H₁₂O₂.

A communication by Brooks ⁶) to another journal contains in substance the same information as that abstracted above, but in addition we take from it the following particulars: in order to establish the existence of oxidase in the flowers, they were crushed below water. The process of crushing must be carried out under exclusion of air, by pouring a layer of paraffin oil upon the water, as otherwise the solution immediately assumes a brown colour. A yellow liquid is then formed, which gives the colour reactions with α-naphthol and p-phenylenediamine that are typical of oxidase. When the solution is heated on the water-bath the activity of the enzyme is destroyed, and it yields no further colour-reactions.

The phenylethyl alcohol which had previously been detected by us as a constituent of champaca oil was also found present in it by Brooks.

Champaca Oil from white flowers (from Michelia longifolia, Bl.), In the papers quoted above, Brooks ⁶) also refers to the oil of white champaca flowers. This oil is dark in colour, and has the following constants: d 0,897, ester v. 180,0, n₅₀ 1,4470. It contains linalool (identified by its b. p. and by oxidation into citral), methyleugenol (identified by oxidation into veratric

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acid, m. p. 179 to 180°) methylethyl acetic acid (identified from the silver-salt), acetic acid, and traces of a phenol with an odour of thymol.

**Chlorocodon root Oil.** According to a letter received by us from the Imperial Biological-Agricultural Institute at Amani, *Chlorocodon Whiteii*, Hook. occurs in German East Africa in the wild state, and is also cultivated there by the planters for the sake of the hairs which cover the seeds. An experimental steam-distillation of the green root from wild-growing plants had yielded crystals, which were forwarded to us for comparison with those which had been prepared by us (Comp. Report October 1911, 33). They proved, in fact, to be identical with the latter. The pink-coloured crude product melted at about 35°; when recrystallised from water it yielded white crystals which, after being dried *in vacuo* over sulphuric acid, melted between 43 and 45°. The crystals prepared by us at the time, after being again recrystallised and dried over sulphuric acid, gave the same m. p. A mixture of our crystals with those received from Amani showed no depression of melting point.

As mentioned by us in our April Report of 1910, p. 173, P. Friedländer has identified the solid body which has been detected in the root of a *Chlorocodon*-species by E. Goulding and R. G. Pelly¹) as *p*-methoxysalicylic aldehyde. Goulding and Pelly²) have isolated by steam-distillation from root recently received by them from Uganda, about 0.25% of this aldehyde. When condensed with aniline in alcoholic solution the aldehyde yields *p*-methoxysalicylideneaniline, a body which separates in crystals in small yellow plates and has m. p. 67 to 68°.

**Oil of Cinnamomum Parthenoxylon.** An oil distilled at Buitenzorg³) from the chips of Selasian wood (from *Cinnamomum Parthenoxylon*, Meissn.) gave the following constants: d1,067, α<sub>d</sub> +1° 3', sap. v. 8,4, ester v. after acet. 11,8.

**Cinnamon Oil, Ceylon (G. Ph. V).** The price of this important article, of which the consumption by our customers has enormously increased, has undergone no change during the past winter, in spite of the fact that the tone of the cinnamon market has been quite firm throughout the season, and that on occasion, as for instance at the close of the year, the prices in Ceylon underwent a decided advance. Cinnamon-chips, which constitute the principal raw material from which Ceylon cinnamon oil is made, have been wholly unaffected by these fluctuations.

A cinnamon leaf oil prepared at Buitenzorg⁴) contained 74% eugenol; sap. v. after acet. 263.

¹) Comp. Report November 1908, 196.
²) Proceed. chem. Soc. 27 (1911), 235.
³) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49. Also comp. Report April 1911, 43.
⁴) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49.
Citronella Oil. With the exception of a few weeks, this article has been able, during the past six months, to maintain the prices at which it stood when our October Report went to press, that is to say from about 1/- to 1/1 cif, with a firm tendency. The reason of this firmness lies probably in part in the decline of the exports as compared with those of the previous year, and in part also in the systematic withholding from the market of the arrivals by the native traders in Matara.

The exports from Ceylon were as follows:

<table>
<thead>
<tr>
<th>Year</th>
<th>Lbs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1911</td>
<td>1,524,275</td>
</tr>
<tr>
<td>1910</td>
<td>1,747,934</td>
</tr>
<tr>
<td>1909</td>
<td>1,512,084</td>
</tr>
<tr>
<td>1908</td>
<td>1,276,965</td>
</tr>
</tbody>
</table>

The fact that in 1911, as compared with 1910, there was a decline in the shipments of about 13% does not necessarily mean that we are faced with a serious falling-off in the supplies or in the output, for, as the figures quoted above show, the shipments in 1911 not only equalled those of 1909, but they even exceeded those of 1908 by about 20%, in spite of the fact that throughout the year 1911 the cry of short supplies was heard.

It is true, however, that the figures for the present year, so far as they are known, again show a considerable decline, for according to the data at hand the shipments up to 12th February 1912 amounted only to 40,223 lbs. as compared with 173,788 lbs. in the corresponding period of last year.

We are unable to judge in how far this decline is ascribable to the policy of reserve adopted by the native traders, but there are good reasons for assuming that it may be attributed in a large measure to speculation. Whether an upward tendency thus artificially produced can be maintained for any length of time the future must show.

Regular supplies of Java citronella oil have reached us from the producing country and no alterations in price of any kind are to be recorded during the period under review. The sale of this oil to soap-makers has dragged greatly during the last few months; on the other hand, considerable quantities have been consumed by our Department of Artificial Odoriferous Substances, as the oil forms the basis of numerous preparations. There has consequently been no heavy accumulation of stock at our works. We are informed that at a recent fire in Amsterdam 5000 kilos Java citronella oil, which had just been landed, and were stored in a shed, have been burnt.
In addition to the bodies which had long been recognised as constituents of citronella oil, *e.g.* citronellal\(^1\), camphene\(^2\), dipentene\(^3\), methylheptenone\(^4\), borneol\(^5\), geraniol\(^6\) and methyleugenol\(^7\), and of valeric acid\(^8\) (in the ester-form), Schimmel & Co., in the year 1899\(^9\), detected in the oil the presence of *l*-limonene, linalool\(^?\) and a light and a heavy dextrorotatory sesquiterpene. We are now able to give the results of an examination of an authentic original oil, which examination has yielded many interesting data on the constitution of this important article of commerce.

The material worked up by us consisted of portions of numerous fractions which had been obtained by fractional distillation from a large parcel of oil.

Methylheptenone was found to be present in the first fractions, which boiled over between 120 and 161\(^{\circ}\). It was separated in the form of the bisulphite compound, and was furthermore identified from the semicarbazone, m. p. 134 to 135\(^{\circ}\). The surmise that esters might also occur in this fraction, which had been entertained at the outset, proved upon saponification to be unfounded. A fraction with the following constants: b. p. 156 to 157,5\(^{\circ}\), \(d_{15^o} 0,8633\), \(\alpha_b - 15^{\circ}31'\), was also tested unsuccessfully for \(\alpha\)-pinene. A series of reactions, partly intended to detect the presence of other terpenes, again confirmed the occurrence in the oil of *l*-camphene. This examination proved to be particularly interesting because in carrying it out we succeeded for the first time in obtaining from citronella oil camphene in the solid form\(^10\) by fractionation. The portions which boiled over between 160 and 163\(^{\circ}\) consisted almost wholly of camphene. In common with the terpene-fractions boiling between 164 and 168\(^{\circ}\) (\(d_{15^o} 0,8670\) to 0,8635; \(\alpha_p - 58^{\circ}13'\) to \(-61^{\circ}14'\)), — in which latter we had at first expected to find sabinene or \(\beta\)-pinene, — the fractions in question, when oxidised with permanganate in alkaline solution by Wallach’s method, yielded camphene camphoric acid, m. p. 142\(^{\circ}\). The oil which had undergone no change during oxidation turned solid in the cooler during the process of steam-distillation, and after being purified from alcohol exhibited all the characteristics of ordinary camphene. It melted between 49 and 50\(^{\circ}\); \([\alpha]_b - 173^{\circ}22'\) (in 10,2\% solution in chloroform). Fractions which boiled between 160 and 168\(^{\circ}\), when treated with glacial acetic acid and sulphuric

\[\text{References:}\]

2) Journ. f. prakt. Chem. II. 49 (1894), 16.
3) Report October 1893, 15.
5) Report April 1894, 17.
7) Report October 1898, 18.
8) Proceed. Americ. pharm. Ass. 35 (1887), 571.
9) Report October 1899, 16.
10) Report April 1903, 84.
acid, yielded principally isobornylacetate, b. p. 70 to 71° (3 to 4 mm.), which upon saponification invariably gave rise to bornol-free isoborneol, m. p. 212°. Similarly, when separate fractions were saturated with hydrochloric acid gas, the principal resulting product was invariably the well-known camphene hydrochloride, m. p. about 148°. In spite of these results, however, we must continue to assume that the camphene-yielding fractions of citronella oil also contain considerable proportions of another terpene, perhaps an isomeric camphene, which eventually, in the case of some of the reactions above referred to, is converted into derivatives of ordinary camphene. It should further be stated that when a fraction (\(d_{150} = 0.8636; \alpha_d = 67°46'\); \(n_{D50} = 1.47009\)) was oxidised with alkaline permanganate under ice-cooling, there occurred besides camphene camphoric acid, traces of an acid melting at 180°, which was not identical with succinic acid.

Attempts to establish the presence of phellandrene in a fraction boiling between 170 and 175° (\(d_{150} = 0.8490; \alpha_d = 57°14'\)) and of sylvestrene in fractions boiling between 180 to 182° and 182 to 186° respectively, only yielded negative results. On the other hand, dipentene was found in all the fractions, and one of them also afforded l-limonene. The tetrabromides of both terpenes gave the characteristic melting points after fractional crystallisation, and the limonene was furthermore identified from the nitrobenzyl derivative, m. p. 92 to 93°. The above-mentioned fraction boiling between 170 and 175° was also tested for \(p\)-cymene, and for this purpose was treated with 1°/o permanganate. The oil which was not attacked, when driven over with steam, had an odour of cymene, but it also possessed a marked optical activity (\(\alpha_d = 61°10'\)) and when further oxidised under heat it yielded no \(p\)-hydroxyisopropyl benzoic acid. In order to test for terpinene, the fractions boiling above 175° were saturated in a solution of glacial acetic acid and ether with hydrochloric acid gas and also with permanganate in the presence of alkali, according to Wallach's method. The former reaction gave a hydrochloride, m. p. 49 to 50°, from which after heating with aniline a hydrocarbon was regenerated which, after distillation over sodium, possessed the following constants: b. p. 180 to 182°, \(d_{150} = 0.8544; \alpha_d = 0°3'\); \(n_{D50} = 1.47821\). This hydrocarbon yielded no nitrosite, but when brominated in chloroform solution it afforded a bromide, m. p. about 123°; and is therefore identical with dipentene. The permanganate oxidation-product, a syrup, could not be distilled in vacuo without decomposition. The crude product showed no inclination to crystallise. Hence it is probable that citronella oil does not contain terpinene.

The interesting discovery was made that after repeated fractionation it was possible to isolate from the portions containing dipentene terpene-mixtures of a very low sp. gr. These mixtures had a peculiar, estragon-like odour and pointed to the presence of a new terpene. Unfortunately
it was impossible to obtain this body in an approximately pure form, or
to identify it from derivatives. Judging from the values disclosed by
combustion it appears to be a terpene C\textsubscript{10}H\textsubscript{16}. In all our experiments
we were compelled to work on mixtures which, whether brominated, redu-
ced, or treated with nitrosylchloride, hydrochloric acid gas, or by other
methods, yielded derivatives of the dipentene, together with some oily
substance. We found, for example, the following constants: b. p. 40
to 41° (4 mm); d\textsubscript{150} 0,8360, 0,8337, 0,8330, 0,8323; α\textsubscript{D} — 32°41' to 23°24';
n\textsubscript{D\textsubscript{500}} 1,48044. When distilled at atmospheric pressure the body becomes
partly resiny. A particularly light fraction (d\textsubscript{150} 0,8315; α\textsubscript{D} — 29°54';
n\textsubscript{D\textsubscript{500}} 1,48287; mol. refr. 46,41, calc. for C\textsubscript{10}H\textsubscript{18}/\textsubscript{2} 45,24) was insoluble in
formic acid and when it was attempted to prepare nitrosates and nitro-
sites did not separate out any solid substances, but only small quantities of
dipentene dihydrochloride.

Repeated attempts at reduction with sodium and alcohol, however,
yielded hydrated hydrocarbons (d\textsubscript{150} 0,8115; 0,8182; 0,8077), but the fact
that in the course of this reaction comparatively numerous resinous pro-
ducts were formed makes it probable that the latter are reduction-products
of dipentene. It was therefore attempted to hydrate the terpene by means
of colloidal palladium. The hydrosol-solution was prepared by Paal's
method, protalbinate of sodium being used as a protective colloid. The
process of reduction was carried out as follows: about 60 g. of the dialysed,
neutral hydrosol solution (containing about 0,45 g. palladium) was allowed
to remain in contact for about 8 hours with 20 g. hydrocarbon (d\textsubscript{150} 0,8315;
α\textsubscript{D} — 29°44') and 120 g. alcohol, during which time hydrogen was passed
in and the mixture was strongly turbinated. The liquid very soon turned
turbid and palladium was separated off. According to its constants the hy-
drocarbon had undergone no perceptible change and it was therefore sub-
jected to a fresh reduction under similar conditions, but with a more
dilute hydrosol solution, containing a little more protective colloid. The
reduction-product was driven off by steam, and distilled as follows:—

\[
\begin{align*}
\text{d}_{150} & \quad \alpha_{D} \\
1. & 41° (5 \text{ mm.}) \ldots \ldots \ldots 0,7989 \quad - 13°28' \\
2. & 41 \text{ to } 43° (5 \text{ mm.}) \ldots 0,8084 \quad - 17°53' \\
\end{align*}
\]

Fr. I had a pronounced odour of lemon. No solid bromide was
obtained, either in carbon tetrachloride or in an amyl alcohol-ether mix-
ture. Neither fraction afforded a nitrosochloride. Oxidation with per-
manganate yielded no products which could readily be identified. The
combustion showed that the body was a hydrated terpene:—

\[
\begin{align*}
\text{0,1534 g. subst.: } & 0,4874 \text{ g. } \text{CO}_3, 0,1778 \text{ g. } \text{H}_2\text{O} \\
\text{Found} & \quad \text{Calc. for } \text{C}_{10}\text{H}_{18} \\
\text{C} & 86,65\% \quad 86,96\% \\
\text{H} & 12,87\% \quad 13,04\% \\
\end{align*}
\]
Another fraction of the citronella oil with a density of 0.8330 (at 15°) and opt. rot. — 29°59', when hydrated according to Enklaar's method and saponified, yielded considerable first runnings and an alcohol possessing the following characters: b. p. 78 to 80° (5 mm.), d₁₅ 0.9180, α₂D — 9°44'. Faint terpineol-like odour. The phenylurethane, at first oily, finally turned solid (m. p. 110 to 111°). Hence the alcohol was impure α-terpineol, owing its generation probably to the dipentene or limonene which was admixed to the fraction. Further particulars concerning the new terpene must be reserved until after subsequent examination.

The fractions with higher boiling points than the terpene fraction consisted chiefly of citronellal, but they contained, besides considerable proportions of borneol, certain other compounds with somewhat characteristic odours, including a body with a peculiar linalool-like aroma, but which was not identical with linalool. We have not yet succeeded in identifying this body from its derivatives. It was discovered in the portions boiling between 81 and 85°, sp. gr. 0.9122, after they had been freed from citronellal with bisulphite, and from borneol by freezing. No phenylurethane was formed, but oxidation with bichromate and sulphuric acid gave rise to citral, b. p. 89 to 91° (3 to 4 mm.). The characteristic citralidene cyanoacetate had m. p. 120 to 121°. Another fraction, b. p. 71 to 75° (d₁₅₀ 0.8982) when acetylated, afforded an oil, b. p. 72 to 74° (4 mm.), with an odour of linalyl acetate, but, again, the saponified product yielded no phenylurethane, although it was oxidisable into citral. From the above it may however be concluded (contrary to our previous experience)¹) that linalool is not a constituent of citronella oil. We hope to be in a position, later on, to make further communications on this subject. The chromic acid oxidation-product mentioned above, which did not react with bisulphite, was found to contain an oil with a thujone-like odour, which reacted in part with semicarbazide. Possibly the semicarbazone recrystallised from methyl alcohol, m. p. 179 to 182°, was a derivative of thujone. We also attempted, by oxidising with permanganate, to prepare from a fraction boiling between 202 and 210° (d₁₅₀ 0.9121), with a faint odour of thujyl alcohol, the thuja keto acid, m. p. 76°, but were unsuccessful.

The high l-borneol content of the succeeding fractions greatly militated against their being tested for other alcohols. Unfortunately our endeavours to eliminate this troublesome product by chemical means, e. g. chloral remained without the desired result. The l-borneol, m. p. 200 to 203°, which was obtained by freezing-out was found, when oximated, to be free from camphor.

In a fraction boiling between 218 and 230°, which had been freed from borneol as far as possible, we ascertained the presence of neral, albeit in inconsiderable proportions. This body was accumulated in an

¹) Report October 1899, 16.
alcohol mixture which had been separated from the solution of the phthalic ester salt by repeated treatment with calcium chloride, and after being again purified by means of phthalic anhydride it was obtained after saponification in the form of an oil, b. p. 98 to 101° (6 to 7 mm.) to which a faint borneol odour still adhered. It was positively identified as nerol from the tetrabromide, m. p. 116 to 118°. The neryl diphenylurethane was not obtained in an entirely pure form; it only melted between 55 and 57°. The oil which contained nerol also contained a compound from which water was given off when distilled under atmospheric pressure. It would seem, however, that citronellol, which should have been present in these fractions, did in fact not occur therein. In lieu of the silver salt of the acid phthalate (m. p. about 126°) which is characteristic of citronellol, repeated examination only afforded in every case the geraniol-derivative melting at 133°. Hence, in corroboration of the results previously obtained by us ¹), it may now be held to be tolerably certain that Ceylon citronella oil contains no free citronellol. But on the other hand we ascertained that citronellol is actually present in the oil in the form of d-citronellol, as esters (for instance, acetic ester), and certainly also as butyric ester, in such proportions, indeed, that it can scarcely be overlooked if the oil is carefully tested. The alcohol was isolated by treating the saponified oil-portions boiling between 86 and 88° and between 88 and 94° (3 to 4 mm.) and sp. gr. 0,8805 to 0,8884 with phthalic anhydride in benzene solution after previous elimination of the geraniol by calcium chloride. The alcohol, which contained small proportions of borneol, showed the following constants: b. p. 84° (3 mm.), d₁₅₀ 0,8725, α₁₅₀ + 0°13'; b. p. 84 to 85° (3 mm.), d₁₅₀ 0,8696, α₁₅₀ + 1°17'. Another sample, which had been further purified from primarily produced formiate possessed the following properties: d₁₅₀ 0,8661, α₁₅₀ + 1°52', nD₂₀ 1,45891, b. p. 92 to 93° (5 mm.). The silver salt of the phthalate possessed the required m. p. of 125 to 126°.

The present examination has also failed to supply any indications of the presence of terpineol in citronella oil. When tested for geranyl acetate it was found that it was possible to accumulate the oil only to a very slight extent by fractionation in vacuo into those portions of which the b. p. would indicate the presence of geranyl acetate (sap. v. 64 to 76), because mixtures of borneol, nerol, geranionl, esters, a hydrocarbon, and others, were present. But in any case, the odour of an acetic ester fraction, b. p. 96 to 98° (4 to 5 mm.), sap. v. 85, together with the fact that the geraniol content was undoubtedly increased after saponification, warranted the conclusion that geranyl acetate was also present in the fraction under examination.

Analysis of the silver salt of the acetic acid boiling at about 120°:

0,2729 g. subst.: 0,1758 g. Ag.

Calc. for C₈H₅AgO₂ 64,67°/₀

Found 64,42°/₀

The acid mixture which was isolated from the saponification liquors of the ester fractions which had served to afford the test for the presence of citronellol, as well as from the higher boiling oil fractions, contained in those of its portions which boiled above 130° an acid of which the b. p. was about 65° (7 mm.). At ordinary pressure this acid passed over constant at 163°; and by its odour likewise it was recognised as n-butyric acid. It solidified into crystals when placed in a freezing mixture. Its chloride boiled between 35 and 36° (7 mm.) and, with ammonia, was converted into n-butyric amide, m. p. 114 to 115°. Valeric acid, which is said to occur in citronella oil, could not be isolated up to the present. The distillation-residue of the acid mixture which remained behind was a solid yellowish acid, crystallising from water in the form of needles, m. p. about 180°; this acid was not identical with veratric acid.

Those portions from the preparation of citronellol which gave no reaction with phthalic anhydride, and of which the b. p. lay between 85 and 90° (4 mm.), contained a hydrocarbon with an odour resembling that of petroleum. By treating this substance with benzoyl chloride and pyridin its alcoholic constituents were eliminated. The body, when heated in vacuo with sodium, possessed the following properties: b. p. 95 to 96° (5 mm.), b. p. 249 to 252°, d₁₅₀ 0,8924, α₀ — 13° 2', n₀ 1,49281. Combustion showed it to consist of a sesquiterpene C₁₅H₂₄, probably contaminated with a slight proportion of methyleugenol, which is well-known to be the principal constituent of the high-boiling fractions of citronella oil. No derivatives such as a nitroso chloride, nitrite, nitrosate or hydrochloride were obtainable. When the body was brominated in chloroform solution there was a strong evolution of hydrobromic acid. In view of the difference in the constants it is questionable whether this body is identical with the light sesquiterpene of citronella oil of which the presence was detected by us several years ago¹). We have not gone into a further examination of the fractions, which consist principally of methyleugenol and of the dextrorotatory sesquiterpene of which the presence has also already been established on a previous occasion.

The examination detailed above has therefore shown that Ceylon citronella oil contains the following bodies in addition to those previously known: a hydrocarbon of low specific gravity (terpene?), a body related to linalool, an alcohol which may be found to be identical with thuyl

¹) Report October 1899, 23.
alcohol, nerol, \( d \)-citronellol (but only in the form of acetic and of \( n \)-butyric ester), geranyl acetate and a high-boiling laevorotatory hydrocarbon \( \text{C}_{18}\text{H}_{24} \).

It is certain that neither linalool nor valeric acid can be counted among the constituents of the oil.

On p. 35 of our last Report we commented upon certain criticisms to which an acetylation-method for citronella oil, published in *The Chemist and Druggist*, had been subjected by C. Kleber. It would appear that the English chemists concerned in the matter have been far from edified by Kleber's criticism, and still less by the fact that we had been so bold as to reproduce its essential features in our Reports, for soon after the publication of our last Report, articles appeared in two English journals\(^1\), and subsequently in an American publication\(^2\), in which our arguments were contradicted in a more or less aggressive manner. Before dealing further with the contents of these articles, we desire to place on record that it is our practice to refer to the published work of other authors purely from an impartial standpoint, taking as our sole guide the importance of the publication, and disregarding altogether whether our references are or are not palatable to third parties. This principle will also continue to guide us in the future.

Our rejoinder to the comments of the English chemists may be compressed within a fairly brief compass, since all these comments are written from the same point of view, and differ from each other only in the tone in which they are couched. With regard to the latter, Mr. Umney, the author of the article in *The Perfum. and Essent. Oil Record*, undoubtedly carries off the palm, for the spiteful manner in which he treats not only the subject under discussion, but also other parts of our Report, is surely without parallel. In fact, we should have altogether abstained from replying to him, were it not that this might be construed as an admission on our part that Mr. Umney's criticisms were justified, and that we do not admit by any means.

Both Umney and Parry continue to defend the standpoint that in the course of the process of acetylation, water is formed, and in proof of this, Umney even sets up a chemical equation which as Kleber\(^3\) observes very pertinently in a rejoinder dealing with the same subject, looks very fine on paper, but unfortunately does not correspond with the facts. For in reality it is not two molecules of alcohol, as Umney and Parry believe to be the case, but one molecule which reacts with 1 molecule acetic anhydride, giving rise to the corresponding ester and acetic acid. In this process, therefore, no water is formed at all, hence the added

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1) *Chemist and Druggist* 79 (1911), 749; Perfum. and Essent. Oil Record 2 (1911), 259.
2) Parry, Americ. Perfumer 6 (1911), 227.
3) Americ. Perfumer 6 (1911), 228.
sodium acetate does not play the part of a dehydrating agent, which Umney and Parry would fain assign to it.

The authors in question also take umbrage at our entire agreement with Kleber's suggestion that for the sake of clearness fused sodium acetate should be prescribed for the acetylation, and they attempt to fight us with our own weapons by pointing out that we ourselves have always recommended dry sodium acetate for this purpose, and that this same substance is mentioned both in the first and in the second edition of our book *The Volatile Oils*. We admit this at once, but with the best will in the world we cannot see that this is inconsistent with our regarding Kleber's recommendation as fully justified, for although to the chemist "dry sodium acetate" may mean the anhydrous salt, we are of opinion that there is no harm whatever in expressing oneself somewhat more clearly and using the term "fused sodium acetate", particularly so since it has been shown that the term "dry" sodium acetate has been misunderstood by American chemists).

We simply do not understand why Messrs. Parry and Umney should look upon Kleber's proposal as if it were so to say a personal insult. In any case we trust they will conclude from our admission that we are always very ready to make concessions when they appear to us to be to the purpose. It was obedience to this principle which caused us at the time (Report April 1910, 154) to advocate the two hours' acetylation of citronella oils after de Jong had drawn attention to the fact that an acetylation of one hour gave too low values.

Fault has also been found with us because we have not adversely criticised Kleber's suggestions relating to the washing-out of the acetylation-mixture, and in this connection also Parry endeavours to convict us of contradictory views by quoting passages from our above-mentioned book. Parry, however, has altogether overlooked the fact that when reproducing Kleber's recommendation in our last Report (p. 36), we referred in a footnote to our book, with the intention — needless to say — of showing that we ourselves do wash out the acetylation-mixture. As it is possible to do this by different methods without thereby altering the acetylation-prescription itself in any way, and without giving rise to errors, there was no reason whatsoever why we should disparage Kleber's method.

But the suggestion made by the English chemists that the acetylated oil should only be saponified for the space of half an hour is a very different matter. We certainly do protest against such a modification, and that on the ground of experiments carried out by us with mixtures of known geraniol- and citronellal-content, which showed that half an hour's heating with semi-normal-potash liquor is not sufficient for purposes of quantitative saponification. We did not specially mention this

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1) Kleber, *ibidem* 229.
at the time of our experiments (Report April 1910, 154) because we regarded it as a matter of course that the oil should be saponified for at least one hour. But as Parry lays stress upon the fact that according to his experience geranyl acetate is completely saponified after half an hour we may further add that this does not apply to isopulegyl acetate, into which citronellal is converted by acetylation. This we have also ascertained by experiment. With a freshly-prepared and carefully purified isopulegyl acetate a constant ester value of 281,9 = 98.7% ester was only obtained after one hour's saponification. When heated for a longer period the value was not increased, whereas after half an hour's saponification the ester value was only 276.3 = 96.7% ester.

We certainly cannot acquit the English chemists of the charge of not having paid sufficient attention to our recent publications, especially to those relating to the acetylation of citronella oil, and when the Editor of The Chemist and Druggist asserts that the acetylation-method of the English chemists is also based upon experiment, we ask where the experiments with mixtures of known geraniol- and citronellal-content which are said to have been made by English chemists are published? For only by such experiments is it possible to solve the question: not by acetylation-tests with citronella oils. In the interests of the subject itself, and in spite of Mr. Umney's indignation, we shall continue deeply to regret the in our view arbitrary deviations on the part of the English chemists from our acetylation-method. It is to be hoped that in further discussions on the subject Mr. Umney will adopt a controversial style which is more becoming and to the point, as we should otherwise feel compelled to refrain from replying to his publications. In order to set his mind at ease we declare once more that we are, and always have been, very sympathetic indeed towards the geraniol-test as such, and that our sole reason for advocating Schimmel's simple and stricter test is because we doubt the possibility of a general commercial application of the geraniol-test for the present (comp. Report April 1911, 45). If, however, Messrs. Umney and Parry should refuse to understand us, and should persist in distorting our statements, we can only admit that we are powerless to prevent it.

Two slight misunderstandings should not be passed unnoticed. The Editor of The Chemist and Druggist appears to believe that in the acetylation of citronella oil the objective is the evaluation of the esters in the oil, whereas in point of fact the purpose of the acetylation is to determine the geraniol- and citronellal-content. And against Kleber's view that warming of the ready washed-out acetylated oil on the water-bath with sodium bisulphate is superfluous, to say the least, Parry quotes the acetylation-method described in the new edition of our book The Volatile Oils (p. 594), in which it is stated, inter alia, that for the purpose of decomposing the excess of acetic anhydride the acetylation-mixture should be
diluted with a little water and warmed for 15 minutes on the water-bath with frequent shaking. We do not quite follow this argumentation.

As already stated above, Kleber has also published a reply to the articles of Parry and Umney, but a bare mention of this fact will suffice here, as quotation would only involve repetition.

In connection with the above we may briefly refer to a paper by Th. H. Durrans\(^1\) in which a special acetylation-method for Java citronella oil is given, as in Durrans' opinion the method of Umney and Parry is only applicable to Ceylon citronella oil. With regard to this we may point out that the method described in our April-Report of last year (p. 46) yields accurate results both with Ceylon and with Java oil.

In the April number of *The Tropical Agriculturist* there appeared an article by N. Wickremaratne on the citronella oil industry in Ceylon, of which abstracts are given in *The Chemist and Druggist* [79 (1911), 443]. From the last-named journal we quote the following details, in which unavoidably a good deal of familiar ground is included. It is estimated that there are at present in Ceylon 40,000 acres under citronella grass, the total number of stills in operation being about 500. Formerly the principal centre of the industry was in the district of Galle, but at present the cultivation of the grass is restricted to the district of Matara and part of the district of Hambantota. Lena-batu grass is chiefly grown. It is very hardy and yields the variety of citronella oil which is characteristic of Ceylon. The seedlings are planted out at distances of from 1 to 2 feet and after 8 months the grass is ripe for cutting, after which cutting can be repeated every third month. It is done by women with an ordinary sickle. The cut grass, after lying in the sun for a day to dry, is taken to the distilleries. If it should be necessary to keep it there for some time before it is distilled care must be taken not to stack it in high heaps, as otherwise fermentation sets in, resulting in a loss of oil. The distillation is carried out on modern principles; earthenware stills, such as were employed many years ago, are now scarcely seen. The size of the stills varies greatly, their capacity ranging from 700 to 2000 lbs. of grass. Ordinarily each plant has two stills, which are worked alternately so that the distilling itself is not interrupted by the emptying and filling of each still. Two charges are worked up daily, each distillation requiring about six hours. The exhausted grass is used as fuel for the boiler.

Cooling is done in the usual way, the length of the condensing-worm varying from 30 to 60 feet. The oil separates from the water in the receiver and is skimmed off with a cup, while the water, as in a Florentine flask, runs off below. Before the oil is placed in tins for shipment it is filtered several times.

\(^1\) Perfum. and Essent. Oil Record 2 (1911), 201.
Wickremaratne estimates the total yield per acre and year (four cuts) at 18,000 lbs. grass and, when the grass is in good condition, at 68 lbs. of oil.

In our April Report of last year (p. 48) we referred to an article on Andropogon- (Cymbopogon-) oils which had appeared in the Circulars and Agricultural Journal of the Royal Botanic Gardens, Ceylon (Vol. V, No. 12, November 1910, 115). The results of the investigations there recorded have since been published also in the Bulletin of the Imperial Institute. [9 (1911), 240, 333.]

According to a communication by the Imperial Institute in London a sample of citronella oil received from the Gold Coast possessed the following characters: \( d_{150^0} = 0.903, \alpha_D = 2^\circ 56', \) total geraniol 76\% (geraniol 33.9\%, citronellal 42.1\%), sol. in 2.8 vols 70\% alcohol and in 1.4 vols 80\% alcohol. The oil was of a pale yellow colour. The parent-plant is thought to be Cymbopogon Winterianus.

Oil from the leaves of Citrus Hystrix. According to Brooks\(^3\), the leaves of Citrus Hystrix, D. C. yield a maximum of 0.08\% of an essential oil possessing the following constants: \( d_{bo} = 0.9150, \alpha_D = -10.50^\circ, \) \( n_{D30^0} = 1.4650, \) sap. v. 50.2. Its odour resembles that of shaddock-leaf oil (vide p. 116).

Oil of Clausena Anisum-olens. As stated in our Report of October 1909 (p. 145), the leaves of Clausena Anisum-olens (Blanco), Merrill possess, according to Bacon, a strong odour of Russian anise, for which reason they, as well as their alcoholic extract, are employed on the Philippines in the preparation of liqueurs. Brooks\(^3\) obtained from the leaves of this Rutaceae a yield of 1.16\% of a colourless oil possessing the following constants: \( d_{bo} = 0.963, \alpha = 0, \) \( n_{D30^0} = 1.5235, \) sap. v. 3.6. It consisted to the extent of from 90 to 95\% of methylchavicol, which was identified by oxidation into homoanisic acid (m. p. 84 to 86\°).

According to Brooks, certain kinds of cigarettes made in the Philippines are scented with the leaves of Clausena Anisum-olens.

Clove Oil. The result of the winter-crop 1911/1912, which even at the time of our last Report promised to be favourable, is probably not over-estimated at 200,000 bales, which is equal to an excess of about 70,000 bales over that of the previous crop. Yet, in spite of these figures, the prices have not receded to the extent expected, which is no doubt to be ascribed to the fact that within the past few weeks somewhat important sales have been effected both in London and in Hamburg. These sales

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2) Philippine Journ. of Sc. 6, A. (1911), 349.
3) Philippine Journ. of Sc. 6, A. (1911), 344.
are probably connected with the circumstance that in view of the result of the crop buyers at first manifested great reluctance in placing orders, but were finally compelled to come into the market in order not to remain bare of supplies. If no unforeseen incidents occur it is likely that the prices will further recede, especially because recent advices depict the present prospects for this year's summer-crop as very favourable. The prices of clove oil were regulated in the course of the winter by the position of cloves, but they were in part maintained owing to the development of a fairly brisk business for delivery. Extremely low and purely speculative offers proceeding from a certain quarter finally caused a feeling of some uncertainty, but it remains to be seen whether these apparently favourable offers will prove in the end to have been of advantage to the consumers. We have our doubts on this point.

The trade in clove-stems has also been fairly brisk. The bulk of this article continues to be used in the manufacture of vanillin, but it appears to us that just at present the price of clove-stems is too high in proportion to that of cloves.

In completion of the already available statistical material we here reproduce the Report on cloves supplied by the German Consulate at Zanzibar. The report, which covers the year 1910, has made its appearance with the customary delay 1).

The exports of cloves from Zanzibar have been as follows: —

<table>
<thead>
<tr>
<th>Year</th>
<th>Quantity (lbs.)</th>
<th>Value (Rupees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1906</td>
<td>15 105 760</td>
<td>5 349 545</td>
</tr>
<tr>
<td>1907</td>
<td>18 214 668</td>
<td>5 941 817</td>
</tr>
<tr>
<td>1908</td>
<td>14 974 872</td>
<td>3 974 398</td>
</tr>
<tr>
<td>1909</td>
<td>20 285 001</td>
<td>4 956 142</td>
</tr>
<tr>
<td>1910</td>
<td>12 783 149</td>
<td>3 802 048</td>
</tr>
</tbody>
</table>

The exports of cloves in 1910 amounted to 25.6% of the total exports. The clove shipments were distributed as follows: —

<table>
<thead>
<tr>
<th>Year</th>
<th>Europe</th>
<th>U. S. A.</th>
<th>Asia</th>
<th>Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1906</td>
<td>8 939 789</td>
<td>717 909</td>
<td>5 355 875</td>
<td>92 192</td>
</tr>
<tr>
<td>1907</td>
<td>10 457 830</td>
<td>1 102 420</td>
<td>6 553 453</td>
<td>100 965</td>
</tr>
<tr>
<td>1908</td>
<td>7 197 375</td>
<td>651 780</td>
<td>7 051 342</td>
<td>74 375</td>
</tr>
<tr>
<td>1909</td>
<td>10 638 889</td>
<td>2 364 940</td>
<td>7 193 252</td>
<td>97 920</td>
</tr>
<tr>
<td>1910</td>
<td>4 800 676</td>
<td>1 096 215</td>
<td>6 758 231</td>
<td>128 019</td>
</tr>
</tbody>
</table>

The exports of cloves in 1910 amounted to 25,6% of the total exports. The clove shipments were distributed as follows: —

<table>
<thead>
<tr>
<th>Year</th>
<th>Europe</th>
<th>U. S. A.</th>
<th>Asia</th>
<th>Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1906</td>
<td>3 176 924</td>
<td>238 975</td>
<td>1 901 368</td>
<td>32 278</td>
</tr>
<tr>
<td>1907</td>
<td>3 387 448</td>
<td>306 061</td>
<td>2 215 262</td>
<td>33 046</td>
</tr>
<tr>
<td>1908</td>
<td>1 894 363</td>
<td>184 578</td>
<td>1 876 332</td>
<td>18 725</td>
</tr>
<tr>
<td>1909</td>
<td>2 596 630</td>
<td>589 911</td>
<td>1 746 728</td>
<td>22 843</td>
</tr>
<tr>
<td>1910</td>
<td>1 323 287</td>
<td>303 592</td>
<td>2 138 243</td>
<td>36 926</td>
</tr>
</tbody>
</table>

1) Deutsches Handelsarchiv, February 1912.
The shipments to European markets were distributed as follows:

<table>
<thead>
<tr>
<th></th>
<th>1906</th>
<th>1907</th>
<th>1908</th>
<th>1909</th>
<th>1910</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotterdam</td>
<td>1,543,310</td>
<td>952,006</td>
<td>560,351</td>
<td>3,007,720</td>
<td>1,685,900</td>
</tr>
<tr>
<td>London</td>
<td>2,650,919</td>
<td>3,298,930</td>
<td>2,283,330</td>
<td>1,592,492</td>
<td>565,829</td>
</tr>
<tr>
<td>Hamburg</td>
<td>3,841,300</td>
<td>5,529,050</td>
<td>3,296,968</td>
<td>4,498,151</td>
<td>2,177,370</td>
</tr>
<tr>
<td>Marseilles</td>
<td>585,760</td>
<td>418,850</td>
<td>894,986</td>
<td>1,041,827</td>
<td>188,467</td>
</tr>
<tr>
<td>Value (Rupees)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotterdam</td>
<td>557,320</td>
<td>295,300</td>
<td>141,704</td>
<td>712,148</td>
<td>432,425</td>
</tr>
<tr>
<td>London</td>
<td>915,629</td>
<td>1,112,693</td>
<td>600,075</td>
<td>405,447</td>
<td>215,019</td>
</tr>
<tr>
<td>Hamburg</td>
<td>1,387,202</td>
<td>1,770,961</td>
<td>886,785</td>
<td>1,111,183</td>
<td>560,317</td>
</tr>
<tr>
<td>Marseilles</td>
<td>207,338</td>
<td>125,867</td>
<td>225,757</td>
<td>250,876</td>
<td>59,251</td>
</tr>
</tbody>
</table>

The percentage-proportion of the principal countries was as follows:

<table>
<thead>
<tr>
<th></th>
<th>1906</th>
<th>1907</th>
<th>1908</th>
<th>1909</th>
<th>1910</th>
</tr>
</thead>
<tbody>
<tr>
<td>India</td>
<td>33.3</td>
<td>36.3</td>
<td>46.0</td>
<td>32.3</td>
<td>55.5</td>
</tr>
<tr>
<td>Germany</td>
<td>25.9</td>
<td>29.8</td>
<td>22.3</td>
<td>25.9</td>
<td>14.75</td>
</tr>
<tr>
<td>Netherlands</td>
<td>10.9</td>
<td>4.9</td>
<td>3.6</td>
<td>13.7</td>
<td>11.4</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>5.4</td>
<td>5.1</td>
<td>4.6</td>
<td>11.4</td>
<td>8.0</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>17.0</td>
<td>18.7</td>
<td>15.1</td>
<td>7.9</td>
<td>5.6</td>
</tr>
<tr>
<td>France</td>
<td>3.8</td>
<td>2.1</td>
<td>5.7</td>
<td>4.7</td>
<td>1.5</td>
</tr>
</tbody>
</table>

As on previous occasions, it is pointed out that the Customs Statistics declare Germany to be the country of destination of all cloves shipped in German bottoms, whereas the B/L is usually made out with option Rotterdam/London. London being the world's market for cloves, the greater part of the cloves shipped to Germany actually goes to London and not to Hamburg.

The following table gives a review of the clove-crops of the last 10 years (the crop season in each case being August—July).

<table>
<thead>
<tr>
<th>Island of</th>
<th>Island of</th>
<th>Total</th>
<th>Average yearly price</th>
<th>Pemba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zanzibar Frasilah</td>
<td>Pembas Frasilah</td>
<td>Frasilah</td>
<td>Rupees</td>
<td>Annas</td>
</tr>
<tr>
<td>1901/02</td>
<td>43,626</td>
<td>321,599</td>
<td>365,225</td>
<td>6</td>
</tr>
<tr>
<td>1902/03</td>
<td>175,420</td>
<td>251,780</td>
<td>427,200</td>
<td>6</td>
</tr>
<tr>
<td>1903/04</td>
<td>28,369</td>
<td>96,792</td>
<td>125,161</td>
<td>13</td>
</tr>
<tr>
<td>1904/05</td>
<td>79,860</td>
<td>675,683</td>
<td>755,543</td>
<td>9</td>
</tr>
<tr>
<td>1905/06</td>
<td>181,536</td>
<td>109,931</td>
<td>291,467</td>
<td>11</td>
</tr>
<tr>
<td>1906/07</td>
<td>56,833</td>
<td>202,633</td>
<td>259,466</td>
<td>13</td>
</tr>
<tr>
<td>1907/08</td>
<td>141,850</td>
<td>299,952</td>
<td>441,802</td>
<td>9</td>
</tr>
<tr>
<td>1908/09</td>
<td>165,733</td>
<td>449,685</td>
<td>615,418</td>
<td>8</td>
</tr>
<tr>
<td>1909/10</td>
<td>160,000</td>
<td>320,000</td>
<td>480,000</td>
<td>9</td>
</tr>
<tr>
<td>1910/11</td>
<td>52,002</td>
<td>139,301</td>
<td>191,303</td>
<td>10</td>
</tr>
</tbody>
</table>

The above prices refer to Pemba-cloves only; the price of Zanzibar-
cloves rules a little higher. The exports of clove-stems in 1910 amounted to 2,304,958 lbs., of the value of 1,85,723 Rupees. They were distributed as follows:

<table>
<thead>
<tr>
<th></th>
<th>1906</th>
<th>1907</th>
<th>1908</th>
<th>1909</th>
<th>1910</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>2,317,305</td>
<td>2,055,415</td>
<td>2,361,964</td>
<td>4,318,057</td>
<td>2,262,293</td>
</tr>
<tr>
<td>U. S. A.</td>
<td>—</td>
<td>179,900</td>
<td>552,160</td>
<td>186,620</td>
<td>—</td>
</tr>
<tr>
<td>Asia</td>
<td>63,056</td>
<td>48,125</td>
<td>34,787</td>
<td>42,035</td>
<td>42,665</td>
</tr>
<tr>
<td>Africa</td>
<td>2,065</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Value (Rupees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>222,608</td>
</tr>
<tr>
<td>U. S. A.</td>
<td>—</td>
</tr>
<tr>
<td>Asia</td>
<td>6,831</td>
</tr>
<tr>
<td>Africa</td>
<td>285</td>
</tr>
</tbody>
</table>

The greater part of the exports in the year under review, as in previous seasons, went to Hamburg.

We have also recently received a sample of the first clove crop from Amani (German East Africa) which yielded 16.6% of an oil possessing the normal properties set forth below: \( d_{150} 1.0558, \alpha_D - 1^\circ 4', n_{D20} 1.53204 \), phenol-content: 92%, soluble in 1.2 vols a.m. 70% alcohol.

A sample consignment of clove-stems from the same place yielded only 5.3% oil, which, however, was equal in quality to the other commercial varieties: \( d_{150} 1.0515, \alpha_D - 0^\circ 58', n_{D20} 1.53461 \), sol. in 1.1 vol. a.m. 70% alcohol. Unfortunately the quantity of oil distilled from the sample was too small to admit of an estimation of its eugenol content.

A few years ago we repeatedly had occasion to describe in our Reports clove-leaf oils from the Seychelles\(^1\)), and we are now also in a position to report on clove oil proper from the same islands, as we have recently received several samples of Seychelles cloves, which we have worked up for oil. Two of these distillates gave the following constants: \( d_{150} 1.0470, 1.0485, \alpha_D - 1^\circ 30', -1^\circ 6' \), phenol content 85 and 86% respectively. Both oils were soluble in 1.5 vols. 70% alcohol, but upon the addition of 4 vols. of the solvent the mixture turned cloudy. In respect of imperfect solubility, therefore, the oils behaved similar to an oil distilled by us from Amboina cloves\(^2\)). This oil, it will be remembered, while behaving normally in other respects, also gave a clear solution at first in 70% alcohol, but solutions of somewhat pronounced turbidity with 3 to 4 vols.

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\(^{1}\) Report October 1907, 37; November 1908, 48.
\(^{2}\) Report October 1904, 22.
Copaiva Balsam Oil. The balsams which are used in the preparation of Pará copaiva balsam oil were occasionally very scarce, and the oil-content of the imports in particular very often left much to be desired. The price has undergone a corresponding increase and appears likely, for the present, to be maintained at the advanced figure. Pará copaiva balsam oil has lately found a regular outlet as an artists' material for painters' use, and appears to be found serviceable for that purpose.

In our Report of October 1910, p. 40, we mentioned a method of testing copaiba balsam recommended by Cocking, which is based, inter alia, upon the feature that the optical rotation of the essential oil separated from genuine balsam is invariably somewhat higher than that of the first 10% distilled from the oil in vacuo. Cocking's method is intended to serve as a means of detecting an addition of African copaiba balsam as well as of Gurjun balsam, and has been recommended for adoption in the British Pharmacopoeia.

Parry\(^1\), while examining several samples of Maracaibo balsam from an undeniably reliable source has found that they did not correspond with Cocking's requirements; on the contrary, in two samples the first 10% of the oil, obtained by steam-distillation, showed a higher optical rotation than that of the bulk of the sample, while in a third sample the two rotations were exactly equal. The optical rotations of the separate fractions of the oils compared with each other also deviated somewhat from the values recorded by Cocking. Parry regards adulteration of the samples examined by him as out of the question, the more so because the deviations were so slight that, if any adulteration were present, it could only have been so small as not to be worth the trouble.

Parry is of opinion that, in order to discover whether Cocking's method is really valuable, it would be necessary to examine a larger number of samples of different origin. If this were done it would of course be necessary also to lay down the conditions of distillation with great precision, and in all cases to carry out the separation of the oil from the resin by steam-distillation, as any other distilling-method would give rise to decomposition-products which would affect the rotation. Parry found that the optical rotation of an oil distilled from the balsam in vacuo was 3,5° lower than that of an oil prepared from the same balsam by steam-distillation.

Cocking\(^2\), in a rejoinder, denies the last-named assertion of Parry's. Cocking has ascertained by experiment that it makes no difference whether the oil is separated from the resin by distillation in steam or in vacuo, and in proof of this contention he quotes the results of comparative ex-

\(^1\) Chemist and Druggist 80 (1912), 19.
\(^2\) Ibidem 128, 204.
periments. The optical rotations, both of the volatile oils and of the cor-
responding fractions, showed but slight differences, the values, taken in
their entirety, being practically the same in each case. For distillation
in vacuo Cocking uses a large splash-head of special design, of which a
sketch is given in his article, and by which any bumping-over of the con-
tents of the flask is obviated. Distillation is continued until the manometer
commences to fall, the fall indicating the commencement of the decom-
position of the distillation-residue.

Cocking again asserts that in his experience the volatile oils from all
genuine copaibas have a higher rotation than the first 10% distilled in vacuo
from them. With several samples which gave the reactions for Gurjun
balsam, and in which the proportion of the adulterant was estimated to
be from 5 to 6%, the distillation-test yielded results similar to those ob-
tained by Parry with Maracaibo balsams.

Coriander Oil. Contrary to all expectations, and in spite of the fact
that the failure of the crop might have been held to warrant a serious
advance, the prices of coriander oil have continued to move within mo-
derate limits. The reason of this is no doubt that the demand for the oil
has fallen off considerably. We have already on a previous occasion
drawn attention to this fact, and recent experience has confirmed our
observation. As a result of this reduced consumption the prices have
remained on the same level as last autumn, and our fear of a further
increase has fortunately not been realized.

Costus Root Oil. We again draw attention to the exquisite oil
distilled by ourselves and we invite our friends to ask us for special
quotations when important quantities are required. We are in a position
to supply costus root oil very cheaply indeed.

In the Seifensieder Zeitung und Revue über die Harz-, Fett- und Öl-
industrie [39 (1912), 160] there is an article by H. Mann on the use of
costus root oil in perfumery from which we take the following: Although
costus root oil imparts a touch of distinction to articles prepared with
it, it is but little used, probably, in part, because it cannot always be
procured. The odour of the freshly-distilled oil is at first not exactly
pleasant, but gradually it develops a most agreeable violet-like aroma,
which also helps to fix other odours. The employment of old oil is not
to be recommended, as it possesses an unpleasant accessory odour,
which easily penetrates other odours, and thus has a predominant effect.
It is advisable to stock the oil in the form of a 10% alcoholic solution.
Used in conjunction with vanillin and Portugal oil in particular it produces
excellent scents. Many French powders owe their popularity to the odour
of costus root oil.

Cubeb Oil. The high prices have remained unchanged, for there has
been no alteration whatever in the position of the cubeb market. The
arrivals are quite insufficient for the requirements, and it is said that numerous former producers have abandoned the cultivation of cubebs because it has not paid them in past years when the prices were low. It might be thought that in the meantime they would have learnt to know better, for the values which have now ruled for cubebs for many years should surely, we think, induce planters to take up the cultivation with renewed energy.

**Cypress Oil.** Since we have taken up in our factory at Barrême the preparation of cypress oil by the method in vogue at our Miltitz works, we have always at our disposal freshly-distilled oil such as we consider necessary for the successful treatment of whooping-cough. Within the past ten years cypress oil has become an indispensable article in the therapy of this disease, its application being as simple as its effect is rapid and completely effective. It is to be hoped that many specialists in this branch of medicine will convince themselves by practical experience of the virtues of this remedy, and we shall always be pleased to supply literature on the subject.

**Dutch Myrtle Oil.** This oil, from *Myrica Gale*, L. (N. O. Myricaceæ), of the constituents of which practically nothing has been known so far, has been subjected to closer investigation by S. S. Pickles\(^1\). A pale yellow oil distilled from a mixture of green leaves and branches (yield 0,076°/o), gave the following constants: \(d_{150} 0,915\), \(\alpha_D - 5^\circ 17'\), acid v. 7,0, sap. v. 31,7, ester v. 24,7. A distillate obtained from half-dried material, almost entirely consisting of leaves (yield 0,203°/o) possessed the following properties: \(d_{150} 0,912\), \(\alpha_D - 11^\circ 26'\), acid v. 4,0, sap. v. 23,2, ester v. 19,2, ester v. after acet. 56,4.

The leaf-oil contained about 0,75°/o of a paraffin \(C_{29}H_{69}\) m. p. 63 to 64°, which separated out in the cold when methyl alcohol was added. By treating the oil with soda solution, Pickles isolated from it about 2,5°/o fatty acids, principally palmitic acid (m. p. 62°). Further constituents are cineole (m. p. of the iodol-compound 112 to 114°) and dipentene (m. p. of the tetrabromide 124 to 125°). The oil contains about 50°/o cineole and terpenes. In addition to the esters of high-molecular fatty acids the oil probably contains a mixture of high-boiling alcohols and sesquiterpenes which, however, has not been more closely examined by Pickles for lack of sufficient material.

Some time ago Laloue\(^2\) published detailed particulars concerning the properties of Dutch myrtle (bog myrtle) oil. Chevalier\(^3\) has tested the pharmacological action of the oil.

**Elecampsane Oil.** So far but little is known of the properties of oil of elecampane, and it may therefore be of interest here to record the

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\(^1\) Journ. chem. Soc. 99 (1911), 1764.

\(^2\) Comp. Report October 1910, 42.
constants of a distillate recently prepared by us from the root of the plant. The product appeared in the form of a mass of colourless needles, saturated with a small proportion of a brown oil, and deliquescent into a brown liquid at from 40 to 45°. Its odour is peculiar, perhaps somewhat like that of ladanum. The high sp. gr. of 1.0374 at 30° and the pronounced optical activity (α₁ + 123° 45′) are worthy of note. The other constants determined by us are: acid v. 6.4, ester v. 180.0, ester v. after acet. 199.0.

Essential Oils, Sicilian and Calabrian.

Our esteemed friend, Mr. Eduardo Jacob of Messina, reports in his customary obliging manner as follows: —

The exports in the year 1911 have exceeded those of the previous year by 187,476 kilos, value 3,709,065 Lire. The shipments have not only absorbed the entire production of the year 1911, but have also reduced from over 100,000 kilos to about 30,000 kilos the stock of old lemon oil which was carried over from the year 1910 into the year 1911. These circumstances gave rise to a general advance in prices in Sicily, until the quotations far exceeded the average of last year. It is not surprising that the first outcome of this advance in prices was that the stocks in foreign countries were used up to the last drop, and the next that during the closing months of the year consumers abroad made their purchases in the producing country with the utmost circumspection and so to speak from hand to mouth only. The fact that in spite of these precautions the stocks in Sicily have likewise been cleared, except for the small balance mentioned above, shows that the world's consumption is steadily expanding. In these circumstances the closing months of 1911 have witnessed an animated business for delivery abroad in 1912, as everywhere there has been a perceptible lack of available oil. The essence trade of Calabria and Sicily has therefore entered upon the year 1912 under exceptionally favourable auspices.

Bergamot Oil. In September of last year this article was quoted at from 42 M to 43 M, and throughout the months of September and October it remained approximately at that level, while the available oil, almost to the last drop, passed into the hands of the consumers.

During the four or six weeks preceding the arrival of the new oil the old stocks had been cleared to such an extent that a few stubborn holders, who up to that time had refused to sell, were able to realize as much as from 50 M to 52 M for their wares.

It is true that on the whole the new crop was not expected to yield a favourable result, but the manufacturers nevertheless believed that by selling at from 40 M to 41 M they were reasonably sure of a decent
# Exports of Essential Oils in the year 1911.

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1911 Kilos 767 373 Lire 15 679 875
1910 Kilos 629 897 Lire 11 970 810

1911 increase Kilos 137 476 Lire 3 709 065
profit, hence at about the middle of October the first sales for delivery were made at these figures.

As soon as the ice was broken and a definite rate of value had been established for the new oil, a large French firm, through its local agent, set about to buy up every parcel of oil for delivery which came into the market, and continued to buy, even at rising prices, until it had secured a supply of about 15,000 kilos.

As a result of this the prices for delivery were rushed up from 41 \( M \) to about 46 \( M \), and they stood at that height when the first new oil came into the market. As is well-known, the ester-content of bergamot oil depends upon the degree of maturity of the fruit. Unripe fruit yields an oil containing between 28 and 32% linalyl acetate; riper and wholly-matured fruit produces an oil of which the ester-content may reach a maximum of from 42 to 44%.

As the standard of value of bergamot oil is its linalyl acetate content, it used, in previous years, to be in the interest of the manufacturer to begin to work up his fruit only when it had reached full maturity. But in the present season the high prices paid for old oil and the strong demand from foreign countries which, for lack of old material, were content to take low-grade new oil, induced the manufacturers to work up their bergamot fruit in a less mature state than formerly, especially in view of the fact that when the fruit is comparatively green its percentage of oil is generally greater than afterwards.

In the past, when the crop was abundant, the consumers were in the habit of preferring high-grade expensive oils to the cheaper low-grade qualities, but this season, owing to the old stocks having been exhausted, there were plenty of buyers who were prepared to accept oils of a lower standard.

The result was that in the month of December a period of great activity set in in the bergamot oil market, during which the manufacturers were able to dispose readily of their new oil at prices ranging from 43 \( M \) to 48 \( M \). All the signs pointed to a further continuation of regular conditions of sale during the manufacturing-season when, in the first days of January, a natural catastrophe upset all previous calculations and estimates.

Violent whirlwinds of a typhoon-like character afflicted the Calabrian coasts on January 3rd and 4th, and again on January 6th and 7th. So great was the force of the storm that almost the whole of the fruit which still remained on the trees was blown down, only a few favoured valleys being saved from the havoc of the elements. In many localities not only was the fruit blown down, but hundreds, if not thousands of trees were uprooted.

It is a familiar fact that the preparation of bergamot oil is a difficult, irksome task, for which appropriate mechanical appliances are necessary. Now, in the short interval which elapses between the falling of the fruit
and the time when, damaged by its fall, it begins to rot, it was impossible to work up the enormous mass of windfalls into oil; the more so because owing to emigration to America there is a constant want of labour in Southern Italy, and there are no means of increasing the available number of hands during the manufacturing season. Hence the oil of many thousands of bergamots has gone to waste, and even the fruit which it was found possible to work up yielded scarcely one-half of an average oil-output, owing to the peel having been injured by the fall. The storms described above have therefore proved a terrible scourge for the fertile districts of Calabria, inflicting serious damage upon most of the manufacturers and causing great financial losses. Another result of the climatic disturbance was that the fruit which had previously been on the trees, almost all in an immature condition, was prevented from ripening and that such oil as was prepared from the windfalls was therefore without exception of a low grade. It may be taken for granted that at least one-half of the crop has had to be worked up in this summary manner and under these unfavourable conditions in the month of January, and that the shortage of oil as compared with the previous estimates may be put as at least 30 to 40%.

It goes without saying that these events brought the manufacturing season to a sudden, premature close, and the consequences of the unfavourable conditions which have prevailed may be summarised in the statement that the crop has yielded barely more than 40 to 45% of a fair average output, and that almost without exception the oil produced is of a very low ester-content. Oils of 37 to 38% ester-content are scarce and only to be found in very small quantities.

It is quite natural that under such disastrous circumstances the market has been subject to unusual fluctuations. On the one hand the manufacturers, without exception, have produced at most one-half of the quantity of oil they had expected to make, on the other the oil produced is of a lower grade than that which they themselves had made contracts to deliver. They have therefore suffered damage in two different ways, and many of them have been unable to observe their obligations towards the exporters. The latter, again, finding that they could not depend upon receiving all the oil they had contracted for, and which they needed to cover their own sales, found themselves compelled to buy elsewhere to cover their requirements, and this state of things led to a wild rushing up of prices, in the course of which the article was forced up within a few weeks from £45.— to £46.— to a parity of £65.—, heavy sacrifices being exacted from the exporters.

Is it surprising, in the circumstances described above, that the sorely-tried manufacturers should now stubbornly insist upon these high prices, in order that the profit upon the small lots of oil still in their possession may help somewhat to alleviate the wounds that have been inflicted upon
them? On the other hand, who shall blame the consumer who, face to face with such quotations, grows more and more chary of buying such an expensive article as bergamot oil, and steadily more inclined to extend friendly consideration to the artificial oils of commerce?

For the reasons above described there is very little satisfaction to be derived at present from the bergamot oil business. The exporter, who is confronted with great difficulties in his dealings with customers abroad, and who is responsible for the quality of his shipments, has very little inducement nowadays to continue trading in an article in which the opportunities for making profit no longer stand in just relation to the chances of losing money. It only remains to be hoped that in the future better crops will bring about an improvement in the market-position, and that the trade in this fine article of commerce may then regain the interest which for the present it has lost in the eyes of all concerned in it.

Within the past few weeks the oil-prices have given way slightly, because in a few isolated instances manufacturers have attempted to realize, but there is a total absence of any desire to buy. The present buying-price of the oil ranges from $\$\$ 60.— to $\$\$ 63.—.

Special stress should be laid upon the fact that oil produced under such unfavourable and abnormal conditions as those of the present season is no match for the product of previous crops, either in respect of quality or of physical constants. Speaking generally, the odour of the present season’s oil leaves as much to be desired as do its ester-content, its rotatory power and its specific gravity. As all the oil has been prepared from more or less immature fruit, the low ester content goes together with a very low sp. gr. and an abnormally high rotation, reaching $+22$ and $23^\circ$ in the case of some few samples.

**Lemon Oil.** This important article has undergone numerous and not unimportant fluctuations in the course of the last seven months. The last crop, as is well-known, had yielded only a poor medium result, while at the commencement of the 1910/1911 season there was a very heavy stock of old oil on hand. The old supplies have served to eke out the deficiencies in the more recent output, and throughout the season there has been an abundant supply available to meet the requirements of the export-trade. In the last Report the causes which, in spite of this plentiful supply, caused the article to advance at the beginning of September to the high level of from $\$\$ 14.50 to $\$\$ 15.— were set forth in detail. Right from the beginning of the present crop opinions have been divided on the subject of its size: the majority of those interested judging it with great optimism, while others declared it to be smaller than the previous crop. Under the influence of these contradictory views a downward tendency declared itself in Messina in the autumn, which strongly affected the prices, both of spot-supplies and of oil for delivery. The
local exporters vied with each other in offering new oil for delivery to customers abroad at lower and lower rates, while the owners of spot oil in Messina tried their best to rid themselves of the stocks in their warehouses.

Local speculators likewise took a hand in the slump, which, however, was in no wise justified by the statistical position of the article, and between the beginning of September and the end of October the price of oil for prompt delivery was depressed from £15.— to £12.—, and that of oil for delivery from £11.— to £10.50. This movement had for its result to make foreign buyers very reticent of buying oil for prompt delivery, and to keep them from giving even to the low prices of oil for delivery the attention which they merited on the intrinsic strength of the situation. It was only, so to speak, on the threshold of the new crop, that is to say when in the month of November the first large shipments of boxed fruit were being shipped abroad, that a view began to spring up that the quantity of fruit on the trees had been generally largely over-estimated, and that in the most favourable case the new crop would only equal that of the previous year.

The spread of this conviction put a stop to the decline of the market, and at this juncture, of course, the upward reaction began to make itself felt, with the result that within a few days’ time new oil for delivery had risen to £10.75. In the beginning of December it had further advanced to £11.—, and until the arrival on the market of the new oil from £12.25 to £12.50 was being paid for available old lemon oil.

In the meantime, the slump during the months of September and October had resulted in local speculators and exporters being caught with large uncovered sales, and when the first deliveries fell due in the month of December both the exporters and the local contractors called for larger quantities of oil than the manufacturers were able to supply.

Whereas in the previous year, at the beginning of the season 1910/1911, there was a balance of over 100,000 kilos of old oil at the disposal of the export-trade, barely 30,000 kilos of old stock was found to be similarly available in December 1911. This scarcity of oil caused a slow tightening of the prices, which recovered to £11.50 in the first half of January.

Early in the second half of January the East- and North-coasts of Sicily were visited by severe gales, which caused enormous quantities of lemons to fall, and also worked serious havoc among the trees. The quantity of fallen fruit was so large that, in order not to lose the whole, a portion of it was used only for the manufacture of citrate of lime, and the idea of working up the fruit for essential oil was given up. This meant a not inconsiderable shortage in the production of lemon oil, and afforded a fresh excuse for advances in the quotations. The price rose rapidly by leaps and bounds to £12.50 at the beginning of February,
and to M 14.25 in the course of the first half of that month. After remaining steady at that figure there was a fresh upward rush early in March to M 14.85, the highest price paid during the present season.

Lemon oil therefore has now regained the level of price at which it stood last September, and there is hardly any room for doubt that the upward tendency would have continued, if the threatened coal-strike in England had not cast its shadow before, chilling the assurance of the bull-party and encouraging the hopes of the numerous section of those traders, both in Sicily and abroad, who had been caught bare of supplies. As a result of the strike, which had broken out in the meantime, the price of lemon oil gave way to the extent of about 0,50 M, and at the time of writing it stands at 14,25 M. It is extraordinarily difficult, this season, to find an answer to the question what will be the future course of the lemon oil market, a question which everyone interested in the article is asking himself.

The statistical returns indicate that, putting it at the highest, the production available for the world's consumption will not exceed that of last year, while it must not be overlooked that in that year the world's requirements not only absorbed the whole of the current crop, but 70000 kilos of old stock in addition. The shipments during the last three months of the present season exceed by 50000 kilos those of the corresponding period of last year, and it is evident that the 30000 kilos or so which were left in stock from the last crop must have gone into consumption, as there has not been enough new oil available to account for the export of such large quantities. During these three months no supplies of new oil worth mentioning can have accumulated here; even at the present time, when three-fourths of the manufacturing season is over, the trade is living from hand to mouth; the manufacturers are in arrears with their deliveries, and several large export firms have only imperfectly fulfilled their delivery-contracts. In the district of Palermo the conditions of the lemon-oil industry appear to be particularly bad this year, for the lemon-crop there has been even scantier than in the other parts of Sicily, and a large part of the inferior fruit is being forwarded thence, packed loose in railway-trucks, to the large cities of Upper Italy for alimentary purposes. Moreover, up to the present the lemon-oil manufacturing industry in this district is not yet in full swing, and is hardly likely to be so this year, for in spite of the high oil-prices the growers are able to obtain better returns by selling their fruit for human consumption in the home-market. The only cause which could conceivably bring about a considerable decline in the oil-prices would be an accumulation of large stocks, and so far there are no indications of any sort pointing to the possibility of such an accumulation either in the near or more distant future. Again, it would appear that foreign countries have not yet laid in the whole of their annual requirements. It seems fair to assume that in these circumstances only
a complete stagnation in the world's trade, whether resulting from war or other causes, can bring about a considerable decline of the lemon oil prices in the coming summer. But so far as can be foreseen there is no prospect of any serious depression in the world's trade. For these reasons there seems to be very little chance of any important decline in the prices just yet, while a continuation of the present level of quotations and the possibility of higher rates appear to be more likely to be realized.

With regard to the prospects of the next crop it is impossible at the present time even to hazard a prognostication. Throughout Southern Italy the winter has been exceptionally mild; the rainfall has been slight, and there has scarcely been any snow lying in the mountains. Owing to the mildness of the weather all trees of the *Citrus* species, with the exception of the bergamot trees, have developed an abundant foliage, by which the favourable development of the blossoms is made possible, but the scarcity of rain and snow and the dryness of the subsoil which is even now noticeable, are disturbing factors which neutralise the hopes mentioned above. The real conditions will only become clear as the spring advances and confirms either the hopes or the fears for the coming crops.

Special reference should be made to the appearance of the so-called blood-lice of the shield-lice species, a pest which within the last two years has visited extensive districts, especially in the immediate neighbourhood of the larger towns of Sicily and Calabria, attacking all the trees of the *Citrus* species and gradually killing them. Mandarin-, bergamot- and lemon-trees appear to be specially liable to the attacks of this pest; the sweet- and bitter-orange trees seem to be better able to resist it. Systematic experiments conducted by the State Schools of Agriculture appear to have resulted in the discovery of suitable antidotes. Unfortunately the remedies which have so far been suggested, all of which consist in the repeated spraying of the whole tree with some insect-killing liquid, are not only difficult of application but considerably increase the cost of cultivation without guaranteeing a cure. This new disease of the *Citrus* trees certainly constitutes a serious danger to our horticulture and to the essential oil industry of Sicily and Calabria. It is to be hoped that Science will soon discover means of conquering and destroying this new pest.

**Mandarin Oil.** This year's mandarin crop has been of fair average quantity. Nevertheless, from the commencement of the season, the prices of mandarin oil have been higher than might have been expected and have maintained a steady level almost without fluctuations. The reason of this is the entire absence of old stock, both here and abroad, which enabled the new oil to find a favourable market at the outset, a condition which is still maintained.

**Orange Oil, Bitter.** In September 1911 the price of last year's bitter orange oil stood at 16 *M*, and as the new crop, in common with that of
sweet oranges, was not a good one, the price of the oil advanced slowly in the course of the winter. There has been no chance for stocks of any importance to accumulate and it is therefore possible that consumers will have to pay higher rates in the future. Generally speaking it would seem that in the course of the last few years the interest in this article had declined.

**Orange Oil, Sweet.** When the new crop arrived the market was wholly bare of supplies. Hence, immediately upon the arrival of the new oil a brisk turnover ensued, which became all the more animated because the orange crop was known to be small. In sympathy with these conditions the oil-prices, from the beginning of the season, showed a slight upward tendency from 17 M to about 18 M. Business only slackened somewhat when some little stock had again accumulated here and when buyers abroad were able to dispose of their shipments, recently-arrived and afloat. Those with expert-knowledge of the market improved this occasion by taking advantage of the receding prices and by buying in the falling market. At last, about Christmas-time, prices reached their lowest ebb and since then, rising by slow degrees, they have again reached a parity of 18 M. The stocks of orange oil are very small and it is most probable that higher prices will rule during the summer months.

**Preparation of the Oils of the Agrumi.**

It is common knowledge that the oils of the agrumi are prepared by expression from the peel. Frequent attempts have been made to find another method of manufacture, but so far without success. The advantage of the present process is that the oil which is gained by expression from the peel conserves in its entirety its pure natural aroma, whereas ordinary steam-distillation (under atmospheric pressure), yields an oil possessing a different odour and of inferior quality. On the other hand the disadvantage of the expression-process is that it requires so much human labour. A further, and in our view a still greater, drawback is that this process leads to the waste of enormous quantities of oil, for it is obvious that by expressing the oil from the peel into a sponge, and again squeezing it out of the sponge into a vessel, only a portion of the oil expressed, and probably only the smaller portion, is actually gained.

The subject is one of not inconsiderable financial importance for Italy. The average annual exports of the oils in question from 1899 to 1908 inclusive amounted to 934,952 kilos, representing a value of 15,350,737 Lire). In 1909 and 1910 they were smaller: 629,897 kilos (value 11,970,810 Lire) in the former and 604,299 kilos (value 11,676,575 Lire) in the latter year.

In some, but probably only isolated, instances, attempts are made to reduce the loss in handling by distilling the expressed peel with water, but, as stated, this method only yields an inferior oil.

Recently, however, Patané and Carelli ¹ have published a report on a new method of working-up lemons which has been proposed by Professors Peratoner and Scarlata. This process has been patented by the two Professors and is published as an essay in the competition for the prizes offered by the Agrumi-industry for the best solution of the problem. It consists in cutting up the lemons into small pieces, and pressing them so thoroughly that the juice, in exuding, carries with it the oil which is liberated by the bursting of the cells in the peel. The acid liquid is then subjected to distillation under diminished pressure at a distilling-temperature not exceeding 60°. The distillation-residue from which the oil has been removed is worked-up for lemon-juice.

Professors Patané and Carelli have applied their process experimentally at the Chemico-Pharmaceutical Institute of the University of Palermo, and have compared the results obtained by them with those which they obtained by hand-pressure by the old method. Parallel-tests yielded, by distillation 0,12 and 0,136%; by hand-pressure 0,115 and 0,16%. So far as the yield is concerned there is therefore no very marked difference between the two methods.

The idea of working at a low distilling-temperature is quite correct, for when the oil evaporates between 50 and 60°, a temperature at which not even the albumen in the cells coagulates, the distillate preserves the pure aroma of the fruit. There will of course remain a slight, although perceptible difference between the odour of this oil and that which has been obtained by pressure, because the expressed oil contains several per cent of non-volatile waxy substances in solution, which temper the sharpness of the aroma.

Being familiar with the injurious influence of high temperatures upon the oils in question, we have for many years past only rectified lemon oil, orange oil, and bergamot oil at the low temperature of 40 and about 50°.

One objection, however, we must be allowed to make against the process of Peratoner and Scarlata: the yield of oil is too low. In our view it is a matter of prime necessity that, even if perhaps not all the existing oil is recovered, at any rate the yield should be materially higher than it is in the hand-pressing process which is now customary. On the other hand the simplification of the process, although it may also be useful, is of decidedly secondary importance.

With a view of obtaining positive information on the possibility of an increased yield we have procured a large quantity of freshly-gathered

lemons, with which we have made several experiments in distilling. We relate below the result of our experience with that method of manipulation only which produced the best results: —

The yellow layer of the peel, which contains the essential oil of the lemon, is removed by peeling. The thin peel which is thus obtained is shredded and bruised mechanically as small as possible. The oily paste is liberally diluted with water and the resulting thin mass is distilled without previous expression, at between 50 and 60 mm. pressure, until the distillate contains not a drop more of oil. All indirect heating with steam-jacket vapour during the distillation must be avoided, and only steam of any desired pressure which passes directly into the liquid should be used. It is not necessary to cohobate the resulting water of distillation; it may be used instead to dilute the paste in the next distilling-operation.

By this process we obtained from the lemons 0,3% by weight of oil with a pure odour, possessing the following properties: —

d₁₅₀ 0,8551, α_D + 55° 30' (α_D of the initial 10% of the distillate + 48°),
    citral 3,4%.

d₁₅₀ 0,8547, α_D + 56° 22' (α_D of the initial 10% of the distillate + 50° 4'),
    citral 4,5%.

The higher the distilling-temperature maintained, the more favourable is the course of the distillation, and the easier it is to increase the output, but at the same time the more the aroma of the oil suffers. On the other hand, a low temperature ensures the purity of odour of the oil, but it also renders the evaporation more difficult, with the result that a smaller proportion of oil, and especially of the less volatile citral, distils over. The most favourable temperature is perhaps about 50°, or (when the temperature of the condensing-water is over 20°) nearer 60°.

Care should be taken to render the distilling apparatus, the condenser and the receivers, as nearly air-tight as possible in order to prevent the air-pump from sucking up too much air through the apparatus, and thus to cause the wastage of oil by volatilisation. For it must be remembered that every gallon of this air is also charged with a gallon of oily vapour saturated at the temperature of the water of condensation, and that this oily vapour is lost.

Owing to the low distilling-temperature the cell-walls of the raw material inside the still retain their natural turgescence for some little time, a circumstance which greatly retards the liberation of the oil from closed cells; hence it is absolutely necessary to disintegrate the peel so thoroughly that every cell is opened.

A yield of 0,3% equals more than twice that obtained by hand-pressing. We believe, however, that with some experience it will be possible to increase still further the output of oil by our process. With water-distillation under diminished pressure the less volatile constituents, especially
when they are to some extent soluble in water, may easily escape evaporation. In the case at issue the valuable citral would thereby be primarily affected. It is certain that at $50^\circ$ only a very small proportion of the citral which has been dissolved in the water will evaporate. Therefore, too much water must not be used in diluting the peel-pulp. On the other hand it is necessary that the boiling mass inside the still should preserve a certain degree of fluidity in order that the inflowing steam may set up an undulating motion in it. For this reason we only distilled the thin upper layer of the peel, and not the entire peel — which would have been simpler and less laborious —, because if the entire peel had been used the increased mass of distilling-material would have required the addition of a far larger proportion of water and would thus have kept more citral in captivity.

Possibly the above particulars may contain some useful hints for the improvement of the Italian agrumi-industry, but we feel it necessary to call attention to another very characteristic difference between distilled oil and hand-pressed oil.

It is common knowledge that oils of lemon and orange can only be kept in good condition for a very limited period, and that after some time they acquire a foreign, acrid odour. If they have been kept in a corked bottle, it will be found that the cork has been bleached pale yellow. Protected from light and air the hand-pressed oils, owing to their wax-like constituents, may be kept for more than a year, but not for several years. It is different with the wax-free distilled oils; their keeping power is much smaller. When the distillation has been conducted under atmospheric pressure by means of water, that is to say at about $100^\circ$, the oil begins to deteriorate after some weeks, or a few months. Oils of lemon and orange which have been distilled at about $50^\circ$ retain their pure odour for a longer period, but, according to our experience, scarcely as long as twelve months.

Bergamot Oil. In the table below we present a symposium of the characters of a series of bergamot oils which have been submitted for our opinion within the past six months and which have proved to be adulterated.

Samples Nos. 1 to 5 contained added terpiny1 acetate, in proportions varying from $14\%$ in No. 1 to about $3\%$ in No. 5. With the exception of the sp. gr. of No. 1, which was too high, the constants of the samples were generally within the limits of the values for pure bergamot oils; hence the adulteration was only demonstrable after fractional saponification. Sample No. 6 was also suspected of containing added terpiny1 acetate, and moreover, contained an ester belonging to the group of esters of sparingly soluble acids, the saponification value of the evaporation-residue and the difference between saponification value and acid value II being
not inconsiderably in excess of the limits of value of pure bergamot oils. It was however impossible to carry out a more detailed examination of this oil, or to identify the ester in question, owing to the insufficiency of the sample submitted.

The altogether abnormal constants of sample No. 7 at once showed it to be adulterated, and even gave rise to the suspicion that it represented not so much a grossly-adulterated oil as an altogether worthless artificial product.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>d&lt;sub&gt;150&lt;/sub&gt;</td>
<td>0.8967</td>
<td>0.8867</td>
<td>0.8833</td>
<td>0.8853</td>
<td>0.8833</td>
<td>0.8795</td>
<td>0.8781</td>
<td>0.8845</td>
</tr>
<tr>
<td>α&lt;sub&gt;0&lt;/sub&gt;</td>
<td>+21°14'</td>
<td>+19°14'</td>
<td>+18°0'</td>
<td>+18°25'</td>
<td>+16°55'</td>
<td>+23°16'</td>
<td>+54°40'</td>
<td>+16°40'</td>
</tr>
<tr>
<td>Evap. Residue</td>
<td>6,5%</td>
<td>4,0%</td>
<td>5,0%</td>
<td>6,4%</td>
<td>4,8%</td>
<td>4,8%</td>
<td>4,8%</td>
<td>5,6%</td>
</tr>
<tr>
<td>Sap. v. of evap. res...</td>
<td>192,5</td>
<td>182,1</td>
<td>170,2</td>
<td>182,0</td>
<td>175,0</td>
<td>221,7</td>
<td>332,4</td>
<td>185,0</td>
</tr>
<tr>
<td>Sol. in 90% alcohol</td>
<td>0,5 vols. a.m.</td>
<td>0,3 vols. a.m.</td>
<td>0,4 vols. a.m.</td>
<td>0,3 vols. a.m.</td>
<td>0,5 vols. a.m.</td>
<td>—</td>
<td>0,2 vols. a.m.</td>
<td></td>
</tr>
<tr>
<td>Acid v.</td>
<td>2,9</td>
<td>1,6</td>
<td>1,5</td>
<td>2,2</td>
<td>1,5</td>
<td>1,2</td>
<td>0,9</td>
<td>1,8</td>
</tr>
<tr>
<td>Ester v. after 1 h. sapon.</td>
<td>99,5</td>
<td>105,7</td>
<td>96,9</td>
<td>101,8</td>
<td>95,0</td>
<td>100,7</td>
<td>—</td>
<td>100,8</td>
</tr>
<tr>
<td>Ester v. after 2 h. sapon.</td>
<td>34,8%</td>
<td>37,0%</td>
<td>33,9%</td>
<td>35,6%</td>
<td>33,2%</td>
<td>35,2%</td>
<td>—</td>
<td>35,3%</td>
</tr>
<tr>
<td>Ester v. after 1 h. sapon.</td>
<td>111,9</td>
<td>114,1</td>
<td>101,6</td>
<td>106,5</td>
<td>98,7</td>
<td>102,9</td>
<td>76,0</td>
<td>103,9</td>
</tr>
<tr>
<td>Ester v. after 2 h. sapon.</td>
<td>87,5</td>
<td>97,7</td>
<td>90,8</td>
<td>97,1</td>
<td>90,7</td>
<td>97,7</td>
<td>61,1</td>
<td>97,5</td>
</tr>
<tr>
<td>Difference</td>
<td>24,4</td>
<td>16,4</td>
<td>10,8</td>
<td>9,4</td>
<td>8,0</td>
<td>5,2</td>
<td>14,9</td>
<td>6,4</td>
</tr>
<tr>
<td>Sap. v.</td>
<td>102,0</td>
<td>107,3</td>
<td>98,4</td>
<td>104,0</td>
<td>96,5</td>
<td>101,9</td>
<td>62,0</td>
<td>102,6</td>
</tr>
<tr>
<td>Acid v. II</td>
<td>91,2</td>
<td>101,0</td>
<td>90,9</td>
<td>97,1</td>
<td>89,8</td>
<td>89,6</td>
<td>52,3</td>
<td>96,4</td>
</tr>
<tr>
<td>Difference</td>
<td>10,8</td>
<td>6,3</td>
<td>7,5</td>
<td>6,9</td>
<td>6,7</td>
<td>12,3</td>
<td>9,7</td>
<td>6,2</td>
</tr>
<tr>
<td>Terpynel acetate content, about:</td>
<td>14%</td>
<td>8%</td>
<td>4%</td>
<td>3,5%</td>
<td>3%</td>
<td>suspect</td>
<td>7%</td>
<td>suspect</td>
</tr>
<tr>
<td>Esters of sparingly soluble acids</td>
<td>Not demonstrable</td>
<td>Not demonstrable</td>
<td>Not demonstrable</td>
<td>demonstr.</td>
<td>demonstr.</td>
<td>about 1%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sample No. 8 contained about 1% glycerol ester and probably, in addition thereto, a small quantity of terpinyi acetate. After having been shaken four times with an equal volume of 50% alcohol (Report April 1911, 150) it was found that the weight had decreased down to 33,6% of the original. Evaporation of the four solutions of the glycerol ester and subsequent fractional distillation in vacuo yielded a few grms. of the ester boiling between 125 and 130° (4 mm.), with the following constants: d<sub>150</sub> 1,1564, α<sub>0</sub> ± 0°, n<sub>D</sub> 1,44317, acid v. 2,8, ester v. 610,6, sol. in about 5 vols. water and more. Estimation of the constituents of the ester showed about 39% glycerol and 64% acetic acid.

In connection with the above we submit the constants of a few samples of bergamot oil in which no foreign esters were detected, but of which
the properties are nevertheless recorded here for the purpose of showing what low-grade products are placed upon the market as the result of the present high price of bergamot oil:

<table>
<thead>
<tr>
<th>d_{150}</th>
<th>α_{p}</th>
<th>Residue of evap.</th>
<th>Solub. in 90% alcohol</th>
<th>Acid v.</th>
<th>Ester v.</th>
<th>Ester (calc. as linalyl acetate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,8812</td>
<td>+22°</td>
<td>4,5%</td>
<td>0,2 vols. a.m.</td>
<td>1,6</td>
<td>76,9</td>
<td>26,9%</td>
</tr>
<tr>
<td>0,8802</td>
<td>+19° 35'</td>
<td>4,4%</td>
<td>0,2 vols. a.m.</td>
<td>2,8</td>
<td>76,5</td>
<td>26,8%</td>
</tr>
<tr>
<td>0,8667</td>
<td>+56° 30'</td>
<td>3,2%</td>
<td>0,5 vols. a.m.</td>
<td>1,5</td>
<td>57,7</td>
<td>20,2%</td>
</tr>
<tr>
<td>0,8710</td>
<td>+30°</td>
<td>—</td>
<td>10 vols. a.m.</td>
<td>1,8</td>
<td>45,7</td>
<td>16,0%</td>
</tr>
<tr>
<td>0,8694</td>
<td>+30° 40'</td>
<td>—</td>
<td>10 vols. a.m.</td>
<td>1,8</td>
<td>36,4</td>
<td>12,7%</td>
</tr>
<tr>
<td>0,8629</td>
<td>+53° 50'</td>
<td>1,7%</td>
<td>4,5 vols. a.m.</td>
<td>0,9</td>
<td>41,1</td>
<td>14,4%</td>
</tr>
</tbody>
</table>

**Lemon Oil.** In our Report of November 1908 (p. 61) we stated that in the examination of a considerable number of samples of authentic lemon oils we had estimated the citral-content by a method which had been communicated to us from a friendly quarter (Dr. Kleber), but which so far had not been published. Comparative tests with mixtures of known citral-content, made at the time, demonstrated the satisfactory character of the method. We ascertained the citral-content of the lemon oils in question to be from 4,3 to 7,2%. Afterwards (Report October 1911, p. 45) we made it known that in its original form the method had given values which, in part, were found to be too high, and that after having improved the method it only showed a citral-content of from 4 to 5%. We are glad that, after a long interval, the publication of a paper by Kleber\(^1\) enables us to give further particulars of the method, and our satisfaction is the greater because expressions of criticism of our prolonged silence have already made themselves heard\(^2\). As however, the method was made known to us in confidence by Dr. Kleber at the time, we did not regard ourselves entitled to publish it. The basis of Kleber's method is the observation that phenylhydrazine (when di-ethyl orange is used as an indicator) gives a sensitive titration with mineral acids, and that with aldehydes and ketones it forms hydrazones which give a neutral reaction with di-ethyl orange. Kleber proceeds as follows:

About 10 g. lemon oil are exactly weighed into a flask, 20 cc. of freshly-prepared 5% alcoholic phenylhydrazine solution are added, the stoppered flask is allowed to stand about half an hour at about 35°, after which as much seminormal hydrochloric acid is added as is required to neutralise the phenylhydrazine solution, the quantity having been previously estimated by a separate test. The mixture is poured into a separator, the flask itself rinsed out with 20 cc. water and the whole vigorously shaken. As soon as the two layers have separated, the lower of the two is drawn off into an titration flask, the residue washed out with

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\(^1\) Americ. Perfumer 6 (1912), 284.

\(^2\) Umney, Perfum. and Essent. Oil Record 2 (1911), 260.
5 cc. water and added after separation of the solution previously run off, and the total contents of the flask titrated with seminormal soda liquor. Di-ethyl orange is used as an indicator and in all cases the titration is made for the brownish tint which precedes the pink coloration. As each cc. of seminormal soda liquor corresponds to 0,076 g. of citral, the citral content of the oil may be calculated from the amount of soda liquor which has been used up.

Kleber found that parallel-tests almost invariably produced exactly corresponding results, and that in the case of mixtures of known composition the difference rarely exceeded 0,1%. As the phenylhydrazine solution decomposes very rapidly, it is best prepared fresh each time; and in no case should a solution be employed which is more than 24 hours old. If necessary, the phenylhydrazine should be rectified beforehand in vacuo.

Kleber has ascertained that his method is also suitable for estimating the citronellal-content of citronella oil, and that it may be specially employed with advantage in the evaluation of Java citronella oil. He found Ceylon citronella oils to contain from about 7 to 9%, and Java oils from about 32 to 37% citronellal, but in view of the limited number of estimations which have thus far been carried out these figures are of course not to be taken as limits of value1). Kleber uses 5 g. Ceylon oil or 2 g. Java oil in his determinations.

Kleber believes that his method may be found generally applicable for the estimation of aldehydes and ketones and leaves it open to his colleagues in research-chemistry to make further experiments in this direction.

We have already stated that Dr. Kleber communicated his method to us privately some considerable time ago and that, as our own experience has shown it to give really practicable results, we are able to recommend it. We ourselves have somewhat modified the method and proceed as follows:—

About 2 cc. oil are mixed with 10 cc. of a freshly-prepared 2% alcoholic phenylhydrazin solution, and allowed to remain undisturbed during 1 hour in a glass-stoppered flask of about 50 cc. capacity. We then add 20 cc. decinormal hydrochloric acid and mix the liquid by gently moving the flask backwards and forwards. After adding 10 cc. benzene the mixture is shaken vigorously and poured into a separating funnel. The acid layer, amounting to about 30 cc., which separates out clearly after the mixture has been left to settle a short time is then filtered in a small filter.

To 20 cc. of this filtrate 10 drops di-ethyl-orange solution (1:2000) are added and the mixture is titrated with decinormal potash liquor until a distinct yellow colour appears. From this the quantity, in cc., of deci-

1) We ourselves have previously found a higher citronellal-content in both these oils by an indirect method of estimation. Further examinations are needed to clear up these contradictory results (Report October 1899, 21, and April 1900, 14).
normal potash liquor required for 30 cc. of the filtrate is calculated. For the purpose of estimating the value of the phenylhydrazine solution a blank test without oil is made in a similar manner. If it is found that the quantity of decinormal potash liquor used up for 30 cc., of the filtrate = a in the first, and = b in the second experiment, it follows that the quantity of citral present in the amount of oil under test (s grms.) equals a — b cc. of decinormal potash liquor. Hence, 1 cc. decinormal potash liquor being equal to 0,0152 g citral, the percentage proportion of citral in the oil is expressed by the following formula

\[
\frac{(a - b) \cdot 1.52}{s}
\]

The object of the extraction with benzene (in which we have followed a suggestion of Kleber) is to re-clarify the solution, which becomes turbid after the addition of the hydrochloric acid. We have observed that when this has been done it is easier to recognise the change in the colour during the titration.

We summarise below the results which we have obtained by this method with mixtures of known citral-content. These figures clearly show the usefulness of the method.

<table>
<thead>
<tr>
<th>Percentage of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
</tr>
<tr>
<td>Found . . . . . . . . . . . .</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

From a paper by Chace¹) we observe that several American chemists have also obtained satisfactory results with Kleber’s process. Comparative determinations by the methods of Chace (Report April 1907, 116), Hiltner (Report October 1910, 163), A. H. Bennett (Report April 1909, 110, October 1909, 153) and Kleber have shown that the last-mentioned method not only appears to afford the best results, but is also the easiest to carry out. The least satisfactory of all were the colorimetric tests; Hiltner’s method regularly gave results below the actual values, Chace’s, above them. In respect of accuracy of results Bennett’s method came next to Kleber’s, but Bennett’s method failed partly in this particular that not all the chemists who applied it were able to recognise beyond a doubt the concluding point of the reaction.

As a result of the experiences set forth above the official chemists of the Bureau of Agriculture of the United States, at their 27th Annual Meeting, agreed to recommend Kleber’s method for the determination

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of citral in oils of lemon and orange. In addition to this they propose the colorimetric method of Hiltner\(^1\)). The citral-content test of orange oil has for its principal object the detection of any added citral or oil of lemon. If the citral-content ascertained by Hiltner's method exceeds 0,7\(^\circ\)/ such an adulteration is probable.

J. R. Rippetoe and L. E. Wise\(^2\)) have also been working at the estimation of citral in oils of lemon. Their reason for taking up this investigation was the desire to substitute another and more reliable method for that of Sadtler (comp. Report April 1904, 48 and October 1904, 119) which has been incorporated in the U. S. Pharmacopoeia. With this object in view they submitted the methods worked out by Chace and Hiltner to control-tests, and they came to the conclusion that Hiltner's method might possibly be suitable for admission into the Pharmacopoeia. In that case, of course, the minimum-content of citral demanded by the Pharmacopoeia would need to be reduced from 4 to about 3,8\(^\circ\)/.

Parry\(^3\)) reports on several shipments of lemon oil adulterated with turpentine oil. The oils in question were distinguished by their abnormally low optical rotation (\(+\) 50 to \(+\) 54\(^\circ\)), and also attracted Parry's attention because their citral value was very low (3,3 to 4,1\(^\circ\)/). Closer examination revealed the presence of copious quantities of pinene, pointing to sophistication with turpentine oil. The comparatively small drop in optical rotation considering the amount of adulterant present leads Parry to think that in every case the adulterant was Greek turpentine oil, which has a high dextro-rotation, and he was confirmed in this view by hearing from Sicily that Greek turpentine oil is used there as an adulterant of lemon oil.

**Orange Oil.** According to Brooks\(^4\)) it would be possible to prepare in the Philippine Islands from the peel of the fruit of *Citrus reticulata*, Blanco, known locally as *naranjita*, an oil which is almost identical with Italian orange oil. *Citrus reticulata* is generally regarded as being synonymous with *C. Aurantium*, L., but Brooks is of opinion that this is not correct. The oil, which was pressed from the green peel, had the following constants: \(\alpha_{D,580} 90,85^\circ (\mp ?)\), \(n_{D,580} 1,4700\), ester v. 8,0, residue of evaporation 2,25 to 2,4\(^\circ\)/. It contained about 92\%/ limonene, about 0,3\%/ of a wax-like stearoptene, m. p. 116 to 117\(^\circ\), 0,5\%/ of an acid (possibly butyric or caprylic acid), and traces of a phenol.

Another *Citrus*-species which is cultivated in the Philippines is *Citrus Aurantium*, Blanco, the fruit of which is locally known as *cajel*. This fruit


\(^2\) Amer. Journ. Pharm. 88 (1911), 558.

\(^3\) Perfum. and Essent. Oil Record 2 (1911), 209.

\(^4\) Philippine Journ. of Sc. 6, A. (1911), 345.
is not suited for the preparation of oil, the yield being too small. The constants of the oil are as follow: $d_2^0 = 0.8390$, $n_D = 1.4675$, sap. v. 8.5.

The precise botanical classification of the two Citrus-species still remains to be determined.

Eucalyptus Oil. There is very little to be said concerning this oil, the market position having undergone hardly any change. Lately, however, the demand for the common Australian variety, which consists chiefly of "amygdalina" oil, has been so keen as to lead to a tightening of prices, but whether the present range of values can be maintained remains to be seen. "Globulus" oil has also been in strong demand, but the chief interest continues to be manifested in our pure eucalyptol, which we are in a position to supply on most favourable terms.

The enormous quantities of eucalyptus oil which have lately been used in the mining districts of Australia in the recovery of zinc and lead sulphides 1), have induced Mr. H. G. Smith the well-known chemist, to enquire whether the Australian Commonwealth will be able to continue to supply sufficient oil to meet the demand 2). At present the gathering of the leaves is still too costly, and moreover the necessary hands for the work are lacking, but Smith is of opinion that this difficulty may be overcome by the use of machines for collecting the raw material, and by the erection of large plant. Generally speaking, he says, the distilling plants are much too small; he has only seen one still (on Kangaroo Island) capable of holding 5000 lbs. of green leaves (of Eucalyptus cneorifolia). The charge from this still can be emptied within 6 minutes, and each distillation yields about 100 lbs. oil. If heating by open hearths were replaced by steam-heating it would be possible, according to Smith, considerably to increase the yield.

We cannot spare the space to refer in detail to the enquiries made by Smith in the different districts, but his report clearly shows that at present the distillation of eucalyptus oil in Australia is not yet conducted on rational principles.


1) Comp. Report April 1911, 72; October 1911, 49.
2) The Technical Gazette of N. S. Wales, of 29/5/1911. From a reprint kindly sent to us.
3) See Report April 1911, 73.
E. Rudder, Maiden, E. Baueriana, Schauer (E. subrotunda, R. Br.; E. polyanthemos, Benth. non Schauer; E. Fletcheri, R. T. Baker with the var. conica, Maiden and E. cneorifolia, D. C. (E. stricta, R. Br. non Sieb.; E. hypericifolia, Link; E. myrtiformis, Naudin [?]).

Oil of Fagara Aubertia, see Oil of Xanthoxylum Aubertia, p. 134.

Oil of Fagara xanthoxyloides. In our last two Reports (April 1911, 73; October 1911, 49) we referred to xanthotoxin, an interesting body which has been found by Thoms in the root oil of Fagara xanthoxyloides. Even at that time, Thoms surmised xanthotoxin to be a coumarin-like compound, related to citroptene. His latest investigations\(^1\) have confirmed the correctness of this supposition. By extracting the shells with alcohol, Thoms obtained a solid substance (m. p. 128\(^\circ\)) which was split up by repeated recrystallisation into two parts, xanthotoxin (m. p. 145 to 146\(^\circ\)) and bergaptene (m. p. 190 to 191\(^\circ\)), the latter a constituent of bergamot oil. The two bodies are isomeric, but bergaptene is a phloroglucinol derivative, whereas xanthotoxin is derived from pyrogallol.

Besides nitroxanthotoxin, which has already been described\(^2\), Thoms prepared methylxanthotoxic acid (m. p. 114 to 117\(^\circ\)) and methylxanthotoxin methylate (m. p. 44\(^\circ\)). The isomeric methylbergaptene methylate melts at 52\(^\circ\). When melted with potash, pyrogallol carboxylic acid is formed, from which it is evident that xanthotoxin is a pyrogallol derivative to which the molecular structure reproduced below applies, assuming that no atomic transposition takes place during the melting-process.

Experiments with sticklebacks showed that the narcotic power of xanthotoxin is considerably higher than that of bergaptene.

From a botanical point of view the occurrence of xanthotoxin and bergaptene in Fagara xanthoxyloides, and of bergaptene in the fruit of Citrus Bergamia, the parent-plant of bergamot oil, is interesting, for the two plants are closely related, belonging to sub-divisions of the same botanical family, namely: Rutaceæ-Xanthoxyleæ and Rutaceæ-Aurantoideæ.

\[
\begin{align*}
\text{OCH}_3 & \quad \text{O} \quad \text{O} \quad \text{CO} \\
\text{HC} & \quad \text{CH} \quad \text{O} \\
\text{CH} & \quad \text{CH} \quad \text{CH}
\end{align*}
\]

Xanthotoxin.

\[
\begin{align*}
\text{CH} & \quad \text{HC} \quad \text{O} \\
\text{OCH}_3 & \quad \text{O} \quad \text{O} \\
\text{CH:CH} & \quad \text{CH:CH}
\end{align*}
\]

One of the formulae

given for bergaptene by Pomeranz\(^3\).

Another body which has been isolated by Thoms and F. Thümen\(^4\) from the root-bark of Fagara xanthoxyloides by extracting with benzene

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\(^{1}\) Berl. Berichte 44 (1911), 3325.

\(^{2}\) Comp. Report October 1911, 50.

\(^{3}\) Monatsh. f. Chem. 12 (1891), 379.

\(^{4}\) Berl. Berichte 44 (1911), 3717.
is fagaramide, m. p. 119 to 120°, which has been identified by the authors as the isobutylamide of piperonylacrylic acid. They prepared the bodies synthetically from piperonylacrylic acid chloride and isobutylamine in ethereal solution. So far, the presence of this nitrogenous body in the oil of *Fagara xanthoxyloides* was unknown.

**Fennel Oil.** Our prophecy that only a slight reduction in the prices of fennel could be looked for in the course of the winter has come true. The farmers, almost without exception, have been able to obtain the prices for which they were standing out, and the oil-distillers in Galicia consequently remained firm in their turn. We have ourselves within the past few months distilled a quantity of fennel, so as not to leave in the lurch the numerous customers who appreciate our “extra” quality with high solidifying-point.

**Garlic Oil.** As is well known, garlic oil \(^1\) is one of the few oils which contain sulphur. According to Manindranath Banerjee\(^2\) a ready method of estimating the sulphur-content is to triturate impure mercury containing lead in a mortar with garlic-juice, when lead sulphide, together with a minute proportion of mercuric sulphide, is formed. It is even possible by this means to free the mercury entirely from lead.

**Geranium Oil.** Since our last Report there has been a further considerable change for the worse in the position of the African geranium oil market. In so far as it was at all possible to procure any offers, the prices ranged between 55 and 60 francs, and these figures have actually been paid for various small lots which turned up here and there. Generally speaking, however, business in the article was extraordinarily quiet, inasmuch as consumers very strongly objected to pay such prices, and instead turned their attention in an increasing degree to substitutes, among which our pure geraniol takes the first place. Whether the high values of oil will induce growers who had abandoned their plantations in previous years on account of the low prices, again to take up geranium growing remains to be seen, but in any case it must be borne in mind that there is no prospect of a return to the old, brisk trading-conditions in geranium oil unless there is a considerable reduction in prices. The total exports of African geranium oil from Algeria in 1911 amounted to

\[
\begin{align*}
28,500 & \text{ kilos, compared with} \\
33,800 & \text{ in 1910,} \\
41,000 & \text{ in 1909,} \\
46,000 & \text{ in 1908.}
\end{align*}
\]

As was to be expected, therefore, the shipments again show a considerable falling-off last year.

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\(^{1}\) Comp. Report October 1910, 68.  
\(^{2}\) Proceed. chem. Soc. 27 (1911), 234.
The position of Réunion geranium oil was uncertain at the time when our last Autumn Report went to press, for one reason because it was too early to say anything about the coming crop, and for another because all sorts of contradictory rumours were current on the probable course of prices. Not until the end of December was it possible to state with some degree of certainty that the summer crop, which commences about this time, was likely to give a favourable result, although in some districts the growing crops had again been damaged by a cyclone. The prices sagged by a few francs, and might perhaps have returned to near their old cheap level, if a well-known Grasse firm had not caused a sudden veering round in the tendency by speculative operations. The quotations thereupon again advanced by leaps and bounds, and it now remains to be seen whether the firm in question will succeed in carrying its speculative interference to a successful issue. Naturally, it is the consumers who pay, for they are compelled nilly-willy to concede the high prices as soon as their stocks are at an end. It is obvious that in these circumstances it is out of the question to pronounce an opinion on the future of the market. For the first time for a long period the exports of Réunion geranium oil show a decline, the shipments from St. Denis having been as follows:

In the year 1911, 45,238 kilos
,, ,, 1910, 64,156 ,, .

Ginger Oil. A few large purchases of suitable distilling material at advantageous prices have enabled us steadily to replenish our stocks of ginger oil, and we have therefore been in a position to cope throughout with the brisk demand which has made itself felt in spite of the high prices. Unfortunately, the general scarcity of the article has undergone no alteration during the past few months, and the position must still be described as very firm.

Gingergrass Oil has been rather neglected, principally because those manufacturers who formerly were in the habit of buying the article regularly, have found in our exquisite palmarosa-oil substitute an adjuvant which is at once cheaper and possessed of a finer odour. Under the pressure of lack of business the prices of the new season's gingergrass oil have receded to a level scarcely ever known in the past. In spite of this little interest is shown in the article, and wholesale transactions are at a standstill.

A sample of this oil distilled at Buitenzorg\(^1\) gave the following constants: \(d_{p} 0,928, \alpha_p +46^\circ 5'.\) The yield was 0,1\(\%\).

Grape Fruit Leaf Oil see Shaddock Leaf Oil, p. 116.

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\(^1\) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49.
**Iva Oil.** With the object of filling-in the somewhat incomplete chemical data available on the subject of iva oil, we have examined in some detail one of our most recent distillates. It had been prepared from the dry flowering herb, the yield being about 0,37% oil of a bluish-green colour and an intense, narcotic odour, which also reminded of valeric aldehyde, cineole and thujone. The constants were as follow: \( d_{150} \) 0,9330, \( n_{D_{200}} \) 1,47607, acid v. 7,5, ester v. 18,7, ester v. after acet. 91,5, sol. in 0,7 vols. and more 70% alcohol, with elimination of paraffin. The presence of an aldehyde (valeraldehyde?), was revealed by the formation of a solid bisulphite-compound when the oil was shaken with bisulphite liquor, but the paucity of the quantity obtained precluded identification. Treatment of the oil with semicarbazide solution yielded a semicarbazone melting at 237,5°, the alcoholic solution of which was dextrorotatory, and which, when decomposed with dilute sulphuric acid, yielded camphor. As was to be expected from the optical behaviour of the semicarbazone, its ethereal solution was laevorotatory, hence there was no doubt of laevo-camphor being a hitherto unknown constituent of iva oil. In addition to this body, the oil appears to possess alcoholic constituents, partly esterified, partly in the free state, as is indicated by the saponification values of the original and the acetylated oil.

**Juniper Berry Oil.** In the course of last winter we have again worked up several wagon-loads of Italian berries, which on the present occasion constituted the most suitable material for our purpose. They were, it is true, dearer than other varieties, but thanks to the abundant oil-yield we were able to leave our selling-prices unaltered. Hungarian juniper berry oil, as a result of the poor harvest, has been quoted from 10 to 15% higher this season than in 1910/1911.

**Ladanum Oil.** This as yet little-known oil\(^1\) is obtained from ladanum resin, which is an exudation of bush-like plants belonging to the genus *Cystus* indigenous to Asia Minor, Crete, Cyprus and a few other islands off the coast of Asia Minor. It has recently been investigated by H. Masson\(^2\), who has found it to contain hydrocarbons, phenols, esters, ketones, and sesquiterpene-compounds. Masson now communicates the results of his investigations of the ketones. He treated a fraction boiling at 85 to 90° (15 mm.) with hydroxylamine hydrochloride, and obtained an oxime with b. p. 133° (16 mm.). From this oxime he regenerated the ketone, which, when purified from primarily produced semicarbazone (m. p. 207°), boiled at 200° (91° at 18 mm.) and was identified as acetophenone by oxidation into benzoic acid. So far this ketone had not been known to occur in volatile oils.

\(^1\) Gildemeister and Hoffmann, *The volatile oils*, p. 505.
\(^2\) Compt. rend. 154 (1912), 517.
A fraction boiling between 70 and 78° (15 mm.) yielded an oxime, m. p. 106° (126 to 127° at 17 mm.) from which Masson obtained a ketone possessing the following properties: b. p. 178 to 179° (66 to 67° at 10 mm.), d₄₀ 0.922, α ± 0°, nD₂₀ 1.4494. This ketone did not react with bisulphite; it yielded a monobromide with m. p. 41° and a semicarbazone with m. p. 220 to 221°. With sodium and moist ether it was capable of being reduced to the corresponding secondary alcohol, which forms large crystals, m. p. 51° (b. p. 87° at 28 mm.). With cold 3% potassium permanganate solution the ketone was oxidised into geric acid (b. p. 190 to 191° at 31 mm.; m. p. of the semicarbazone 164°), the latter, when oxidised with sodium hypobromite, giving rise to bromoform and α,α-dimethyladipic acid. This process of resolution has therefore shown the ketone C₉H₁₆O to be trimethyl-1,5,5-hexanone-6, a body which has not been described up to the present.

\[
\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C(CH}_3)_2 \cdot \text{CO}_2 \text{H}
\]

Geranic acid.

\[
\text{CH}_3 \\
\text{CH} \\
\text{H}_2 \text{C} \\
\text{CO} \\
\text{H}_2 \text{C} \\
\text{C(CH}_3)_2 \\
\text{CH}_2
\]

Trimethyl-1,5,5-hexanone-6.

**Laurel Oil.** This article is suffering from decided over-production, and we desire earnestly to impress upon the producers the need of a reasonable moderation of output, for there is simply no outlet for such quantities as have recently been offered from Palestine and the Greek islands. The unwholesome position of the market has been correspondingly reflected in the downward course of prices.

**Lavender Oil.** We regret to report that our fears have been realized, for in October and November the French dealers began to enter the market as buyers with such vigour that within a brief space of time the prices were driven up to 42 francs for oils of high quality. Fortunately, by that time we had already secured the greater part of our requirements (which always exceed the capacity of production of our Barrême works), and we may therefore leave to others whatever claims to distinction there may be in having driven up values without any particular reason. The principal stocks in producers' hands quickly found buyers at the prices indicated, and what supplies now remain in the first hand are either unimportant or of inferior quality. It is true, however, that the demand soon began to droop once more and that for the past three months practically no sales have been effected. In any case there are at present no
signs whatever of an important change in the market, be it upwards or downwards, within the next few months, and it is too early of course to hazard an opinion concerning the coming crop. Generally speaking the rainy winter-weather has favoured the development of the plants.

F. Delphin has published two articles calling attention to two new lavender oil adulterants which have come under his notice. In the one case he concludes that in all probability the adulterant was cocoa-nut ether, although the acid which was separated out from the lavender oil in question, while possessing the same acid value as the acid from cocoa-nut ether, showed a decidedly higher iodine value and a somewhat lower m. p. These discrepancies, however, were to be explained by residual impurities from the lavender oil.

In the second case, Delphin found phthalic ester to have been the adulterant. The acid which was separated out from the saponified oil, after being purified and several times recrystallised, melted at 198,5° with evolution of gas (phthalic acid from the anhydride melting in a similar manner at 198°) and gave the same reactions as phthalic acid.

By applying the method proposed in our Report of October 1910, p. 61, an adulteration with the esters in question (which belong to the esters of sparingly-volatile acids) would be detected, in the course of the determination of the difference between the saponification value and acid value II, by the increase in this difference. It would therefore be impossible to overlook it, and all that would remain to be done would be the identification of the acid in question.

In connection with the above we print a table containing the analytical values of a few samples of lavender oil submitted to us for our opinion. Sample No. 3 in this table is especially worthy of note, because here the abnormally low acid value II (with the corresponding excessive difference), together with the result of the test for terpinyl acetate and glyceryl esters appeared to point to sophistication, whereas in reality they were the result of a resinification. In such cases the sample in question should be rectified with steam. Renewed testing, together with the determination of the distillation-residue (which, in the case under review amounted to 8°/0), will then show whether the cause is adulteration or resinification.

As regards sample No. 5, with an ester-content of 51°/0, it is hardly necessary to point out that when 10 cc. seminormal potash liquor are used the required excess of alkali is too small, and that for that reason 15 cc. should be used. It follows that, to obviate erroneous conclusions in the test for terpinyl acetate, 30 or 15 cc. should then be employed under otherwise similar conditions.

1) Svensk Farmaceutisk tidskrift 1908, No. 22; 1912, No. 5. From a reprint kindly sent to us.
Samples No. 1 and 2 contained terpinyl acetate, while No. 4 was adulterated with glycercyl ester, which was detected by shaking with 5% alcohol. 10 cc. of the filtrate obtained in accordance with the method described in our Report of April 1911, p. 150, used up 0,91 cc. seminormal liquor. It was not possible, however, to identify the glycercyl acetate, the sample at our disposal being too small.

L. Lamothe, to whose publications on lavender, its cultivation and its distillation, we have already repeatedly referred in these Reports, calls attention in an interesting article to the fact which up to the present has been but little noticed, namely the increasing cultivation and utilisation of lavandin (Lavandula fragrans × latifolia, Chatenier). This species, which is the result of a crossing of lavender and spike, is known in Southern France by several other names besides "lavandin", for instance "lavande bâtarde", "grosse lavande", "badasse", and others.

<table>
<thead>
<tr>
<th>Lavender Oil</th>
<th>No. 1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
<td>Dist.</td>
<td>Original</td>
<td>Shaken</td>
<td>15 cc.</td>
</tr>
<tr>
<td></td>
<td>oil</td>
<td>with</td>
<td>oil</td>
<td>once with</td>
<td>seminormal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>steam</td>
<td></td>
<td>5% alc.</td>
<td>liquor</td>
</tr>
<tr>
<td>d₁₅₀</td>
<td>0,9007</td>
<td>0,8946</td>
<td>0,9072</td>
<td>0,8932</td>
<td>0,8992</td>
</tr>
<tr>
<td>α₀</td>
<td>-3°35'</td>
<td>-2°34'</td>
<td>-5°14'</td>
<td>-5°37'</td>
<td>-4°32'</td>
</tr>
<tr>
<td>Solub. in 70% alcohol</td>
<td>2,5 Vol. a.m.</td>
<td>2,5 Vol. a.m.</td>
<td>1,9 Vol. a.m.</td>
<td>2,2 Vol. a.m.</td>
<td>2,5 Vol. a.m.</td>
</tr>
<tr>
<td>Acid v.</td>
<td>0,3</td>
<td>0,5</td>
<td>0,8</td>
<td>—</td>
<td>0,5</td>
</tr>
<tr>
<td>Ester v. after 1 h. sap. with 10 cc.</td>
<td>78,4</td>
<td>83,3</td>
<td>100,5</td>
<td>102,5</td>
<td>90,0</td>
</tr>
<tr>
<td>1/2 n. liquor</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ester content (calc. for linalyl ac.)</td>
<td>27,4%</td>
<td>29,2%</td>
<td>35,2%</td>
<td>35,9%</td>
<td>31,5%</td>
</tr>
<tr>
<td>Ester v. after 2 h. sap. with 20 cc.</td>
<td>82,7</td>
<td>87,6</td>
<td>104,2</td>
<td>104,6</td>
<td>91,9</td>
</tr>
<tr>
<td>1/2 n. liquor</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ester v. after 1 h. sap. with 10 cc.</td>
<td>69,7</td>
<td>77,0</td>
<td>99,0</td>
<td>100,6</td>
<td>91,1</td>
</tr>
<tr>
<td>1/2 n. liquor + 25 cc. alc.</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Difference</td>
<td>13,0</td>
<td>10,6</td>
<td>5,2</td>
<td>4,0</td>
<td>0,8</td>
</tr>
<tr>
<td>Sap. v.</td>
<td>78,7</td>
<td>83,8</td>
<td>101,3</td>
<td>102,5</td>
<td>90,5</td>
</tr>
<tr>
<td>Acid v. II</td>
<td>75,7</td>
<td>83,7</td>
<td>96,7</td>
<td>100,6</td>
<td>90,6</td>
</tr>
<tr>
<td>Difference</td>
<td>3,0</td>
<td>0,1</td>
<td>4,6</td>
<td>1,9</td>
<td>—</td>
</tr>
<tr>
<td>Terpinyl acet. content about</td>
<td>5%</td>
<td>4%</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Esters of spar. vol. acids</td>
<td>not ascertainable</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Glyceryl ester</td>
<td>not ascertainable</td>
<td>doubtful</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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1) Report November 1908, 76; April 1909, 62; October 1911, 58.
2) Parfumerie moderne 5 (1912), 9.
3) For further details see the original article, and also the same author’s pamphlet “Lavande et Spic” (Report November 1908, 76). Also compare A. Birckenstock, “Action de l'hybridation sur les essences de lavande et aspic” (Report October 1906, 43).
4) Lamothe also gives “grande lavande” as a synonym, and frequently uses this designation for “lavandin” in his article. On the other hand in his brochure "Lavande et Spic", he expressly differentiates between “grande lavande” (spike), and “grosse lavande” (lavandin).
Its flowers develop about a fortnight later in the season than those of the true lavender, which is ascribable to its hybrid character; spike, for example, flowers still later, in the beginning of September. Lavandin occurs principally in the region of the holm-oak, and even spreads beyond the boundaries of the latter, traversing in a broad belt the Departments of the Drôme, Vaucluse, Basses-Alpes, &c., where it covers the southern slopes of several mountains up to the top.

Like all hybrids, lavandin is an extraordinarily hardy plant, and in its prolific development constitutes an actual danger to the true lavender, which it robs of air and nourishment. The fact that this hybrid is gaining ground year by year gives cause for serious concern, the more so because pasturing sheep and goats shun it on account of its acrid odour and bitter taste, whereas in the true lavender these animals find an occasional welcome substitute for grass.

But in spite of this same bitter, herbaceous and camphor-like flavour, which places it far behind lavender as an odoriferous plant, very considerable quantities of lavandin are cut for distilling.

Lamothe estimates that the lavandin oil which is brought to market every year amounts to about 20 p. c. of the total output of lavender oil or, in weight, to about 12,000 kilos. He regards this as most regrettable and utters an emphatic warning against the distillation of lavandin flowers, for although they yield a better return than true lavender, and with less trouble, their oil is decidedly inferior and may easily injure the present predominant position of French lavender oil. Lamothe gives a very interesting comparison of the respective outputs, which deserves to be quoted here. In the same time which is required to collect about 55 kilos true lavender flowers nearly 400 kilos of the freer-flowering lavandin can be gathered without trouble. And whereas for the production of one kilo lavender oil 145 kilos flowers are needed, from 77 to 80 kilos flowers suffice to produce one kilo of lavandin oil.

With regard to the properties of lavandin oil Lamothe states that the samples distilled by him had an average ester-content of 24°/c. As in the case of true lavender oil a linalyl acetate content of 30°/c is considered low, this fact shows the inferiority of lavandin oil; but by estimating the ester-content it is always possible to guard against the use of an inferior product.

Lamothe not only warns his countrymen against the distillation of lavandin flowers, but also against their export, because here also the reputation of French lavender is likely to suffer as a result of the poor quality of these flowers. He has no doubt that such frauds are practised,

1) Compare Report October 1906, 44. A sample of "lavandin" oil examined by us gave the following constants: \(d_150\ 0.8911, \alpha = 3.25°\), ester v. 51,5 = 18°/c ester (calc. as linalyl acetate), sol. in 2 vols. a. m. 70°/c alcohol.
for many unscrupulous dealers are found who are in the habit of mixing flowers exhausted by distillation with the fresh lavender.

Lamothe advocates the total and permanent exclusion of the hybrid from all commercial uses, but at the same time he suggests that on account of its profusion in flowering and its hardy character it shall be given a place of honour as an ornamental plant.

E. Th. Brewis and J. C. Umney report on the changes which English lavender oil undergoes under certain circumstances during storing. The reason for the investigation was the fact that as a result of the high prices now ruling, supplies were being placed upon the English market which showed quite abnormal characters, indicating a percentage of esters so high as to lead to the idea that the oils were mixed with French oils. A more careful investigation, however, showed that the samples merely represented old oils which had become much resinified as the result of years of keeping. The oils were instantly distinguishable by their unpleasant, resinous, acetic odour. They also had an exceptionally high sp. gr., and in most cases the proportion of free acid and ester was uncommonly large. The sp. gr. varied according to the degree of resinification, the maximum being 0,9885, the acidity varied up to 3,22% (calc. as acetic acid) and the ester-content up to 22,7% (calc. as linalyl acetate). The corresponding values of normal oils were as follow: d150 0,884 to 0,896, acidity 0, in one instance 0,12%, ester content 5,9 to 11%.

In view of the fact that the degree of resinification was independent of the age of the oils (a few oils even giving normal constants after more than 10 years' keeping), Brewes and Umney consider that the changes are connected with the percentage of moisture remaining in the oil, all essential oils containing a certain percentage of water dating from the time of their distillation. They are now engaged in studying the matter from this point of view, and they regard it as necessary that more attention should be given to the drying and storing of the oils than has been done at present.

The Bulletin of the Imperial Institute [9 (1911), p. 401] contains an article on lavender-growing in England. As we have only lately dealt at some length with the cultivation of lavender at Mitcham and in other districts of England, we will content ourselves with a mere reference to the article in question.

Lemongrass Oil. With the exception of a short period of pronounced dulness which occurred in December, the tendency of this important article has been firm throughout the last few months. The quotations fell from

1) Perfum. and Essent. Oil Record 3 (1912), 5.
2) Quoted from Journ. Board Agric. U. K. 18 (1911), 566.
3) Report October 1910, 75.
$4^{3/4}$ d. per oz. in October to about $3^{1/4}$ d. per oz. in December, but afterwards they returned to their present level of about $4^{1/2}$ d. per oz. It is said that the stocks in India have shrunk within a small compass, and it is therefore probable that for some time to come a rising market will prevail. The only statistical figures available are as follows:

Shipments of lemongrass oil from Cochin in the period between 1st July and 31st January.

<table>
<thead>
<tr>
<th></th>
<th>1911/12</th>
<th>1910/11</th>
</tr>
</thead>
<tbody>
<tr>
<td>To London</td>
<td>681 cases</td>
<td>676 cases</td>
</tr>
<tr>
<td>Hâvre</td>
<td>1343</td>
<td>1158</td>
</tr>
<tr>
<td>Marseilles</td>
<td>3491</td>
<td>1538</td>
</tr>
<tr>
<td>Bremen</td>
<td>183</td>
<td>250</td>
</tr>
<tr>
<td>Hamburg</td>
<td>893</td>
<td>765</td>
</tr>
<tr>
<td>New York</td>
<td>972</td>
<td>235</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>7563 cases</td>
<td>4622 cases</td>
</tr>
</tbody>
</table>

Although the above figures only give a very approximate clue to the consumption, for the size of the cases differs greatly, it is nevertheless remarkable that the shipments to Hâvre and Marseilles far exceed those to the other ports. We believe this fact to warrant the inference that the present principal consumers of lemongrass oil are France and Switzerland. It will also be seen that the exports in 1911/12 have considerably increased as compared with those of 1910/11.

The Imperial Institute in London\(^1\) reports on several samples of lemongrass oil of different origin. The oils came from Ceylon, India, Uganda, Bermuda, and Montserrat. As, with one exception, we have already referred to the Ceylon oils (Report April 1911, 79), a bare mention may here suffice. It only needs to be added that the samples of this oil described by the Imperial Institute, in common with the distillates of *Cymbopogon citratus* previously mentioned, belong to the class of sparingly-soluble lemongrass oils. The oils from the other localities belong to the same group; an oil from Cochin alone being more readily soluble. This oil the Imperial Institute classes among the "soluble" lemongrass oils, although even with 90\% alcohol it did not afford a solution which remained clear when diluted. It is true that, differing in this respect from the other oils, it gave a clear solution with 2 vols. 70\% alcohol, but even this solution turns turbid when more of the solvent is added. The other constants of the oils are set forth in the subjoined table p. 90.

The distillation of lemongrass oil in Uganda was undertaken at first by Government, and in the year 1909/10 the export amounted to 16603 ozs.

\(^1\) Bull. Imp. Inst. 9 (1911), 334.
of a value of £72. The preparation of the oil has now been taken up by a business-house. The parent plant, according to a determination made at the London Botanical Gardens, is *Cymbopogon citratus*, which accounts for the imperfect solubility of the oil.

We have previously described a lemongrass oil from Uganda (Report April 1909, 65).

<table>
<thead>
<tr>
<th>Origin</th>
<th>$d_{15}^o$</th>
<th>$\alpha_D$</th>
<th>Citral content (Bisulphite method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceylon</td>
<td>0.9058</td>
<td>$-0^\circ 6'$</td>
<td>76%</td>
</tr>
<tr>
<td>India, Tyrna</td>
<td>0.9021</td>
<td>$-0^\circ 20'$</td>
<td>72.5%</td>
</tr>
<tr>
<td>&quot; Cochin</td>
<td>0.9053</td>
<td>$-0^\circ 39'$</td>
<td>84.5%</td>
</tr>
<tr>
<td>&quot; Mariani</td>
<td>0.9140</td>
<td>$-0^\circ 5'$</td>
<td>73%</td>
</tr>
<tr>
<td>Uganda</td>
<td>0.870 to 0.894</td>
<td>$+0^\circ 10'$ to $-0^\circ 24'$</td>
<td>64.5 to 75%</td>
</tr>
<tr>
<td>Bermuda</td>
<td>0.8689</td>
<td>$-0^\circ 21'$</td>
<td>40%</td>
</tr>
<tr>
<td>Montserrat</td>
<td>-</td>
<td>-</td>
<td>over 74%</td>
</tr>
</tbody>
</table>

Brooks\(^1\) describes the oil of an as yet unknown *Andropogon*-species which is evidently closely allied to lemongrass oil. The constants of the oil were as follow: $d_{15}^o = 0.8777$, $\alpha = 0$, $n_{D30} = 1.4868$, and it contained about 72% citral (m. p. of the semicarbazone 155 to 160°) and 12% geraniol. The latter was isolated by means of the calcium chloride compound.

**Limette Oil.** We have recently received from our well-tried, reliable source of supply fresh shipments of the finest hand-pressed oil, so that up to the present we have been able to satisfy the requirements of the numerous customers who have been attracted in the course of years by our exquisite quality. Unfortunately the shipments have been less plentiful of late, and we have therefore already been compelled to increase our prices. The demand for our terpeneless limette oil has also been very animated.

**Oil of Limnophila.** According to Brooks\(^2\) the leaves of a species of *Limnophila* (N. O. Scrophulariaceæ), which occurs in the Philippines, yield about 0.2% of an oil with a rosemary-like odour and a density of 0.850.

**Linaloe Oil.** The market in Mexican linaloe oil has been greatly neglected throughout the winter months, but in spite of this there has been no decline in prices worth mentioning. The main reason for the great neglect of the article must no doubt be sought in the competition of the exquisite Cayenne linaloe oil, which was obtainable at remarkably cheap rates and of which the quality is far superior to that of the Mexican.

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1) Philippine Journ. of Sc. 6, A. (1911), 351.
2) Philippine Journ. of Sc. 6, A. (1911), 345.
oil. The difference in price between the two oils being only small, those who, like ourselves, consume large quantities of the oil in the manufacture of linalol and linalyl acetate, prefer the Cayenne oil to the other. A few parcels of Mexican oil consigned to Hamburg were moreover of such inferior quality as hardly to deserve the name of linaloe oil. The shippers in Cayenne continued to complain of the low prices, but in the end there was no other course open to them but to sell their oil at the price of the day, unless they wished to have it thrown on their hands. But at the beginning of February a serious rise took place in bergamot oil, and suddenly such a demand set in for linalyl acetate and other substitutes that the linaloe oil market recovered within a few days. In the end 19 M was asked for Mexican oil, while Cayenne oil rose quickly from 19 francs cif. Havre to 30 francs. Thus far the prices of both oils have been maintained at this level, and the demand remains exceedingly keen; their further course will mainly depend upon the position of the bergamot oil market. We understand that at a selling price of 19 to 20 francs the manufacture of Cayenne linaloe oil is far from paying, especially because of late, owing to the drying-up of the water-courses, the conveyance of the wood from the primeval forest to the distilling-place has become difficult. In how far the revolution which is now again spreading in Mexico will affect the linaloe oil market is a problem for the future. According to a report by the British Vice-Consul in Cayenne, the exports of linaloe oil from French Guiana have been as follows:

<table>
<thead>
<tr>
<th>Year</th>
<th>Kilos</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1908</td>
<td>7470</td>
<td>186750</td>
</tr>
<tr>
<td>1909</td>
<td>12497</td>
<td>312400</td>
</tr>
<tr>
<td>1910</td>
<td>22066</td>
<td>551650</td>
</tr>
</tbody>
</table>

These figures clearly show the enormous increase of the linaloe oil industry in Cayenne.

The distillation of a large quantity of Cayenne linaloe wood afforded us an occasion for investigating more closely the distillation-waters as well as the first runnings of the oil. The cohabation-water still contains considerable proportions of oil, and especially of linalool, and in addition to these there occur two aldehydes which have already been observed on several occasions in the distillation-water or in the first runnings, or both, of essential oils. These aldehydes are furfural and, possibly, isovaleraldehyde. We isolated the furfural by treating the oil obtained from the cohabation-water with bisulphite liquor. The aldehyde boiled between 159 and 161° and had d_{150} 1,160; with β-naphthylamine it gave the well-known colour-reaction; the phenylhydradrazone melted between 96 and 98° and the semicarbazone at 196°. In comparison with furfural the first runnings only contain very small proportions of isovaleraldehyde. Judging from the irritating, cough-compelling odour and from the b. p. (90 to 95°)
it is most probably present. The thiosemicarbazone had no uniform m. p., as it was impossible to remove the small quantities of furfural which were present.

The cohabation-oil, when freed from its aldehydes, contained, in addition to methylheptenol (Report October 1911, 60), cineole, which we identified from its iodol-compound, m. p. 110 to 111° and its constants; and dipentene, of which the dihydrochloride melted between 47 and 48° and the tetrabromide between 124 and 125°. The cineole-content of the first runnings varied between 30 to 40°/o.

In addition to cineole and dipentene, the first runnings appears to contain an aliphatic terpene. It was impossible to isolate this body by fractionation; by acting upon it with glacial acetic and sulphuric acids we obtained a yield of about 10% of an ester of which the alcohol, after saponification, melted between 210 and 215°, and had d150 0,915. This alcohol resinified very readily; its odour reminded both of linalool and of terpineol. As the fraction with m. p. 168 to 170°, which had been used for hydration, contained no sabinene, camphene, fenchene, or pinene, the surmise that the alcohol has been generated from an aliphatic terpene is probably not quite unfounded.

The observations recorded above are in agreement with the detection in Mexican linaloe oil of an olefinic terpene, announced by us a few years ago (Report April 1909, 67). It is highly probable that this body is identical with myrcene.

In our Report of October 1910 (pp. 26 and 79) we mentioned that a so-called linaloe oil had recently been prepared in Formosa. We have since learnt from the Chemiker-Zeitung1) that a licence for preparing this oil has been granted to the firm of Mitsui Bussan Kaisha, who hope to distil 300 kilos of the oil before March 31st of this year. No further news has been received regarding the botanical origin of the product.

We believe the oil to be probably identical with apopin oil (described in our Reports of October 1903, 10 and April 1904, 10) or with a fraction of that oil.

On the preparation of dihydrolinalool from methylheptenone of various origin, see p. 177.

Oil of Magnolia glauca. The leaves of this North American shrub (Magnolia glauca, L.; N. O. Magnoliaceae) contain, according to a communication by F. Rabak2) 0,05% of a pale-yellow essential oil: d60 0,9240, [α]D +3,96°, nD50 1,4992, acid v. 1,8, ester v. 13, ester v. after acet. 28, gives a cloudy solution in 3 1/2 vols. 90% alcohol, insoluble in 80% alcohol.

1) Chem. Ztg. 36 (1912), 89.
2) Midland Drugg. and pharm. Review 45 (1911), 486.
Melaleuca Oils. In our last April Report (p. 81) we referred to the oils of Melaleuca trichostachya and bracteata, which Baker and Smith had discussed in a paper read before the Royal Society of N. S. Wales. Since then the authors have published more precise details on these distillates1), from which we abstract the following: Oil of Melaleuca trichostachya, Lindl.2) is obtained from the dry leaves, the yield being from 1,25 to 2,580/, and the constants as follow: d₁₅₀ 0,9144 to 0,9153, αₕ + 2,3 to 3,1°, n₁₃₀ 1,4636 to 1,4655, sap. v. 2,1 to 2,8, ester v. after acet. 13,9, soluble in 1,3 vols 70%/ alcohol. In addition to about 80% cineole (determined by the resorcinol method), the oil probably contains pinene. As regards esters, the authors proved the occurrence of terpinyl acetate; they identified the terpineol from the reaction with hydriodic acid (formation of dipentene dihydridiole, m. p. 77°). The oil further contains traces of phenols and of low-boiling aldehydes, as well as a sesquiterpene(3), sp. gr. 0,934; n₀ 1,4985.

Oil of Melaleuca bracteata, F. v. M. This oil, which is prepared from the leaves and branches (yield 0,643 to 0,9640/) possesses the following constants: d₁₈₀ 1,032 to d₁₉₀ 1,0358, α₀ — 1,4 to — 3,1, n₁₃₀ 1,5325 to 1,535, acid v. 0,7 to 1,26, sap. v. 5,3 to 20,8. Ester v. of the saponified oil after acet. 24,57, sol. in 0,7 to 0,8 vols. 70%/ alcohol. It contains 0,36%/ eugenol (m. p. of the benzoyl compound 68 to 69°), 0,33%/ free cinnamic acid as well as cinnamic acid in combination (m. p. 133°), traces of cinnamic aldehyde, a little l-phellandrene (m. p. of the nitrite 120°), cinnamyl-cinnamate (3), and 70%/ methyl eugenol (estimated by Zeisel's method), identified from its bromide, m. p. 77 to 78°, and from oxidation into veratric acid, m. p. 178 to 179°.

Mr. Baker was kind enough to send us, together with a reprint of his paper, a sample of oil of Melaleuca bracteata. It was of a yellowish colour and possessed an agreeable odour, reminding somewhat of champaca oil. d₁₈₀ 1,0422; α₀ — 1° 10'; n₁₃₀ 1,53428; acid v. 0,4; ester v. 20,8; ester v. after acet. 31,0; sol. in 1,5 vols. a. m. 70%/ alcohol.

The leaves of Melaleuca stypheloides, Sm. also afforded an essential oil, but in such exceptionally small proportions that it was impossible to determine its constants.

Oil of Micromeria japonica, Miq. According to Y. Muragama3) the air-dried herb of this labiate contains 0,7%/ of a yellow oil, with a characteristic odour of peppermint. Fractional distillation of the oil yielded l-menthone, which was identified from its boiling point, combustion and the preparation of the oxime. It is possible that the oil also contains menthol.

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1) Journ. and Proceed. Royal Soc. of N. S. Wales 44 (1911), 592. From a copy kindly sent to us.

2) According to Baker and Smith, Melaleuca trichostachya and pinariifolia are not synonymus, as stated in the Index Kewensis, but represent distinct species.

**Mustard Oil.** Contrary to expectation, the demand for the natural distilled oil has not declined to the extent which we anticipated in our last Report, and we have therefore only recently commenced the distillation of another large parcel of mustard seed. It is a fact, however, that there is less demand for natural mustard oil than formerly, and only Russia still remains a regular customer for quantities of some importance. Generally speaking users have turned to the artificial mustard oil, and in this they are quite justified.

It has often been asserted that black mustard does not contain enough myrosin to split up the whole of the glucoside sinigrin which also occurs in it, and in order to increase the yield it has even been recommended to add white mustard during the process of fermentation. Experiments in this direction which have been made by H. J. Greenish and Dorothy J. Bartlett¹) have shown the assumption with regard to the insufficiency of myrosin to be incorrect. Not only does the seed contain enough myrosin to split up the sinigrin which is also present in it, but the proportion of the enzyme is occasionally large enough to decompose thirteen times the quantity of sinigrin in the seed.

As was to be expected, the addition of white mustard during fermentation does not improve the oil-yield in the slightest degree.

According to Greenish and Miss Bartlett the addition of sodium fluoride to mustard seed during fermentation (as recommended by Brioux)⁵), is very effective, 0,4% of the fluoride being sufficient. Fluoride of sodium does not injuriously affect the action of myrosin, but it kills the micro-organisms which destroy the allyl sulphocyanate.

Interesting also is the observation made by Greenish and Miss Bartlett that black mustard of the 1905 crop when examined in 1911 showed a normal myrosin-content; from which it appears that myrosin is not injured by prolonged storage of the raw material.

**Myrtle Oil.** To the myrtle oils of special origin which have been described in our previous Reports⁶) must be added an Algerian oil which has recently been examined by us. Its properties agree with those of the Corsican oil: \(d_{150}^0 0,8871, \alpha_D^{25°} 52^\circ, n_{D20°} 1,46466\), acid v. 1,1, ester v. 20,6, ester v. after acet. 39,2, sol. in 0,5 vol. a. m. 90% alcohol.

**Oil of Nepeta Nepetella.** *Nepeta Nepetella*, L. is the name of a Labiate which grows fairly plentifully in the neighbourhood of Saint-Auba-Dorothy J. Bartlett (Maritime Alps)⁴). The plant possesses a peculiar odour of peppermint. The oil (yield 0,0598%), distilled after the close of the flowering season,

¹) *Pharmaceutical Journ.* 88 (1912), 203.
²) *Annales de Chimie analytique* 17 (1912), 6.
³) *Report* April 1909, 71; April 1910, 78; October 1911, 61.
⁴) *Berichte von Roure-Bertrand Fils*, October 1911, 41.
was heavier than water and constituted a yellow, somewhat viscous liquid possessing the following properties: $d_{20}^0 1.03984$, $d_{20}^0 1.02536$, $\alpha_D + 15^\circ 12'$, $\alpha_D$ of the acetylated oil $+ 17^\circ 20'$, acid v. 45.5, ester v. 245.7, ester v. after acetylation 314.5. It was soluble in 2 vols. 70% alcohol; when more alcohol was added the mixture turned cloudy. A solid body with an odour of menthol was isolated from the oil; the saponification-liquor, after being acidulated, yielded an oil possessing an odour of caprylic and of valeric acid at the same time. Only a portion of the oil was absorbed with bisulphite.

Neroli Oil. It is many years since the winter-rainfall on the Mediterranean coast of France has been so heavy as that of last season, and the trees have therefore been flourishing. As a result of the wet weather, however, some of them have already flowered prematurely during the early months of the year, and these will show a proportionate deficiency during the flowering-time proper in the month of May, but taking it all-in-all the prospects are highly favourable, and unless night-frosts should supervene a good medium-crop may be expected with certainty. There can be no doubt, however, that the yield will not approach that of last season, which was well above the average. At the moment the buds look very healthy and it may be expected that, barring unforeseen circumstances, the gathering will this season commence about 15th April, that is to say about a fortnight sooner than usual. It is thought that the flower-prices will not rule high: at present the talk is of 65 to 70 centimes, for both of neroli oil and of orange flower water there is some stock left over from the year 1911. Naturally, however, the Société coopérative de production des propriétaires d'orangers des Alpes-Maritimes will energetically defend the interests of its members, and will distil all the flowers which it is unable to place with the manufacturers at remunerative prices. For the present it is of course impossible to say much concerning the probable course of the neroli oil prices, which have remained unchanged, with slight fluctuations, throughout the past winter. In the year 1911 the Société coopérative harvested 1800000 kilos flowers, or about 500000 kilos more than usual. Of this output, the Society was compelled to distil about 550000 kilos, because there was no market for this surplus, but the Society was able to dispose of the bulk of the oil thus obtained at prices ranging from 475 to 500 francs per kilo. Just at present there is more pressure to sell, and from several quarters there have been forecasts of a price of about 30 francs for oil of the new crop. The flower-production of the Société coopérative is estimated at rather more than two-thirds of the total flower-crop in the Department of the Maritime Alps; hence it would seem that the total yield of the orange flower crop of the year 1911 has been about 2600000 kilos.

The sale of our artificial neroli oil "Schimmel & Co." last year attained a magnitude previously unthought-of, and as there is now a large number
of regular users of this splendid substitute who formerly absolutely refused to have anything to do with it, it may be confidently anticipated that this article will continue to grow in favour, no matter whether the prices of true neroli oil rise or fall. In the matter of uniformity of quality our artificial neroli oil is decidedly superior to the natural oil.

**Nigella Oil.** Damasceninic acid, a derivative of damascenine, which is a constituent of nigella oil, has been obtained synthetically by A. J. Ewins ¹ from \( m \)-hydroxybenzoic acid by a series of reactions represented below. As Keller ² has shown that it is possible to convert damasceninic acid into damascenine, it follows that the last-named body may be prepared synthetically by Ewins' method.

```
OH       OCH₃       OCH₃       OCH₃       OCH₃       OCH₃
\( \text{COOH} \rightarrow \text{CO}_₂\text{H} \rightarrow \text{NO}_₂ \rightarrow \text{CO}_₂\text{H} \rightarrow \text{CO}_₂\text{H} \rightarrow \text{CO}_₂\text{H} \)
```

\( m \)-Hydroxybenzoic acid.

Nutmeg oil. There has been no lack of nutmegs rich in oil and suitable for distilling purposes. We have again worked up several large parcels and have thus been in a position to replenish our stocks, which had been greatly depleted by brisk sales during the months of November and December, and particularly by large orders from the United States.

**Nutmeg-tree Bark Oil.** At Buitenzorg ³ the sap v. of this oil (which has been mentioned by us on a previous occasion)⁴ has been determined at 14; ester v. after acet. 37,5. The oil contained no aldehydes.

**Oil of Ocimum sanctum.** Some time ago we stated ⁵ that, according to Bacon, the oil of *Ocimum sanctum*, L. contains considerable quantities methylchavicol. Brooks ⁶, who has recently investigated the product, also found methylchavicol to be its principal constituent (50 to 60%\(^{o}\)), besides which he found cineole and linalool present. The cineole afforded the characteristic hydrobromic acid compound.

**Origanum Oil.** An oil of *Origanum hirtum*, Link., which shows a marked similarity to an oil from the same parent plant which has been examined by us ⁷, is described by S. S. Pickles ⁸. The raw material, which

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¹) Proceed. chem. Soc. 27 (1911), 277.
²) Comp. Report April 1908, 73.
³) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 49.
⁴) Report April 1911, 83.
⁵) Report April 1911, 83.
⁶) Philippine Journ. of Sc. 6, A. (1911), 345.
⁷) Report October 1911, 63.
⁸) Proceed. chem. Soc. 27 (1911), 284. See also Bull. Imp. Inst. 9 (1911), 388.
was obtained from Trieste, yielded 3,3/o oil: \( d_{15^0} 0,9440, \alpha_d + 0^\circ 24', \) soluble in 2,8 vols. 70/o alcohol. It contained from 66 to 67/o thymol.

Another sample of origanum herb, which had been received from Trieste by the Imperial Institute in London, and was found to be derived from *Origanum Onites*, L., yielded upon distillation an oil of precisely similar properties to those of a distillate from the same plant described by us a year ago (Report April 1911, 85): \( d_{15^0} 0,9483, \alpha_d — 1^\circ 15', \) sol. in 2,75 parts a. m. 70/o alcohol. The phenol-content, consisting almost entirely of carvacrol, was 68/o.

Orris Oil. Business in both varieties of orris oil has been somewhat sluggish lately, and only began to show signs of revival when it became known that the stocks of Florentine orris root were unusually small and when prices, consequently, began to tighten. The following passage is translated literally from the report of our local correspondents:

"Since our last report on Florentine orris root the prices have continually risen, a result of numerous orders which heavily reduced the existing stocks. According to our previous communications the supply was as follows:—

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stock in hand at end of August 1911</td>
<td>90 tons</td>
</tr>
<tr>
<td>Add 1911 crop</td>
<td></td>
</tr>
<tr>
<td>Total: about 690 tons,</td>
<td></td>
</tr>
<tr>
<td>against which must be set off the total deli-</td>
<td></td>
</tr>
<tr>
<td>veries from the beginning of September 1911</td>
<td></td>
</tr>
<tr>
<td>until the end of February 1912</td>
<td>570</td>
</tr>
<tr>
<td>Hence the available stock on 29th February</td>
<td></td>
</tr>
<tr>
<td>1912 amounted to</td>
<td></td>
</tr>
<tr>
<td>about 120 tons.</td>
<td></td>
</tr>
</tbody>
</table>

The present market price is £ 90,— per 100 kilos cif. Hamburg for sorts; of pickings scarcely anything is left. According to our last report the average annual exports for the nine years from September 1902/August 1903 to September 1910/August 1911 amounted to about 690 tons, as compared with an average crop in the eight years 1903 to 1910 of about 650 tons. The crop of 1911, amounting to about 600 tons only (the raw root yielded fully 20/o less of trimmed root this year than last, apparently owing to the great drought), reduces the average yield of the nine crop-years 1903 to 1911 to about 644 tons. On the other hand the deliveries during the last half-year, from the beginning of September 1911 until the end of February 1912, have been very considerable, amounting to about 570 tons, and it may be taken as fairly certain that when the new crop begins to arrive on the market at the end of August there will be no old supplies whatsoever left to start the new season with. As regards the next crop, the estimates so far agree that it will not only not exceed the last in quantity but will even fall considerably below it."

In view of the conditions presented above, we are compelled to accept the probability of a considerable advance in the price of orris oil within

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1) Bull. Imp. Inst. 9 (1911), 388.
the next few months, and we therefore advise those of our customers who desire to take advantage of our present selling-prices, which are based upon our previous purchases of raw material, to lay in their supplies in good time.

**Parsley Oil from seed.** Raw material suitable for distillation has been very hard to find as, owing to the severe drought, but little seed had been gathered last year. When suddenly an animated demand for parsley oil arose from France the prices advanced considerably, but owing to the small stocks available only a small part of this demand could be satisfied.

**Oil of Parthenium argentatum.** *Parthenium argentatum*, Gray (N. O. Compositæ), a native of Mexico, is an interesting plant, for, as we learn from a paper by P. Alexander, it yields (calculation based upon dry substance), from about 8 to 10% of rubber-material (the Guayule-rubber of commerce), whereas the rubber-content of *Hevea brasiliensis*, the parent-plant of the Pará rubber, can only amount to a few 0/°00 of its total weight. The comparatively high rubber-content of *Parthenium argentatum* is explained by the fact that, as is the case in all rubber-yielding plants, the cells containing the milky juice occur exclusively within the tissues of the bark. In a dwarf-shrub, such as *Parthenium argentatum*, this tissue constitutes a considerable proportion of the entire plant, whereas in a giant tree such as *Hevea* it only amounts to a fraction of the whole weight.

In addition to rubber the plant, calculation based upon dry material, contains about 0,5% essential oil.

For the purpose of preparing this oil material grown in Mexico was used which had probably been collected and dried quite shortly before shipping. It yielded about 0,015% of a greenish-yellow, faintly laevorotatory oil, (d_15° 0,8861), consisting entirely of hydrocarbons. Under fractional distillation at 17 mm. 30% passed over between 50 and 60°; 20,3% between 60 and 80°, and 24,8% between 120 and 160°; the residue amounting to 5,5%. The oil contained l-α-pinene (m. p. of the nitrosochloride 100 to 102°; m. p. of the nitrobenzylamine 122°) and a constituent with a pepper-like odour, the latter being the carrier of the odoriferous substance of the oil: b. p. 130 to 140° (17 mm.), d_15° 0,9349, [α]_D_15° — 21°24', n_D15° 1,496. Alexander surmises this body to be a sesquiterpene, but he was unable to identify it with any of the known sesquiterpenes.

Another oil, distilled from material which had been in warehouse for some considerable time, proved to be rich in oxygen and, when distilled, left a residue of about 50% resin.

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1) Berl. Berichte 44 (1911), 2320.
2) The scanty oil-yield is due to the fact that no suitable distilling-plant for large-scale work was available.
At the conclusion of his paper Alexander pronounces oil of *Parthenium argentatum* to possess a marked similarity to oil of German chamomile. We are unable to judge in how far the odour of the two oils is similar, but they certainly differ altogether in their chemical constitution.

**Patchouli Oil.** This important article, too, gives rise to little comment upon the present occasion. The serious advance in price of patchouli leaves has so far been without material effect upon the price of patchouli oil, although the supplies are beginning to be light. It would seem, however, as if in all quarters ample supplies had been laid in of this article, the value of which notoriously improves with keeping; at any rate the demand moves within very moderate limits. It is also evident that the consumers have at last adopted our view that the patchouli oil distilled in Europe by careful and scientific methods is superior in aroma to that imported from Java and the Straits Settlements, for the parcels of oil which have been imported during the last few months have been very difficult to place, notwithstanding the reductions in price conceded by the owners.

We have referred in previous Reports to de Jong's investigations\(^1\) into the oil-content of patchouly leaves in various stages of development, and it will therefore be sufficient here to state the fact that de Jong has recently published another paper on the subject\(^2\).

**Pennyroyal Oil.** There has been no change recently in the neglected condition of the market for this oil; the demand is extremely small, and in the producing countries but little interest is now shown in the article, because the output of the last few crops has only been saleable at a very moderate profit, if not at an actual loss.

American pennyroyal oil, from *Hedeoma pulegoides*, Pers., as prescribed by the U. S. Pharmacopoeia, has remained scarce throughout the period under review, and the supplies will scarcely hold out until the new crop comes in. Quite recently, according to a communication received from our New York branch, an oil described as "false Pennyroyal Oil", which reminds strongly of rosemary oil, has repeatedly been offered from the Southern States. We hope to be in a position, later on, to give some information concerning the botanical origin of this oil.

\(^1\) The *Pharmaceutical Journal* [87 (1911), 652, 700] contains an article on the etymology of the term "Penny" in the word "Pennyroyal". It is thought that this term may be a corruption of the word "pulliol", the Old English designation of the pennyroyal mint being "Pulliol Royal".

\(^2\) Comp. Report November 1909, 95; October 1909, 92.

\(^3\) Recueil trav. chim. des P.-B. 30 (1911), 211. From a reprint kindly sent to us.
Pepper Oil. We have been afforded an opportunity of securing several large parcels of raw material at advantageous prices, and have thus been able once more to replenish our stocks for some considerable time ahead. We have proportionately reduced the price, but we are further prepared to quote special rates to any customers who are prepared to consider the purchase of quantities of some importance.

Peppermint Oil, American. Our New York expert is of opinion that the firmness of this oil during the whole of the past year is due in the first instance to the fact that even before the crop was ripe a few of the dealers had made large contracts with the principal farmers at comparatively high prices. These contracts kept up the quotations and thus helped to tide over a somewhat dull period, which set in when it was found that, after all, the distilling had yielded a larger output than had originally been expected. The total production of oil in 1911 is now estimated at 240000 lbs. In the late autumn and in the winter a brisk demand made itself felt, resulting in a large turnover at rising prices, which, however, did not deter consumers in the United States. The stocks now in the hands of the producers, amounting to only about 30000 lbs. together with the quantity still left in second hand, will hardly be sufficient to cover the requirements until the arrival of the new crop. For this reason the view prevails in America that an increase in prices may be looked for within the next few months as soon as any considerable demand arises, or if buyers should fail to observe the necessary caution. As is well-known, the trade in American peppermint oil in Europe is dominated by our well-tried brand of rectified oil "F S & Co." This trade has been in a thoroughly satisfactory condition throughout the whole of last year. We were able to supply our principal customers in good time on advantageous terms, and the turnover considerably exceeded that of previous years.

It is still too soon to express an opinion on the effect of the long and severe winter upon the peppermint-fields, but if the spring-weather should be favourable and no late frosts should hurt the roots, the tightening of prices which is to be expected will doubtless induce the growers to extend the cultivation. It will therefore be advisable not to lay in supplies beyond July or August at the present prices.

Peppermint Oil, English. The position is unchanged, and the expected advance has not taken place. In fact, consumers are becoming more and more convinced that this article is much too dear at the present prices, and for this reason they are turning in an increasing measure towards our American brand "F S & Co." As a result of the painstaking method of selection practised by our New York branch the quality of the last-named brand has within the past few years been brought to a degree of excellence which is able to satisfy the most exacting requirements with
respect to pure peppermint-aroma. So far no reports are available concerning the condition of the peppermint-plantations in England.

**Peppermint Oil, French.** The cultivated species of *Mentha*, and in particular *Mentha piperita*, have been examined botanically by A. and E. G. Camus\(^1\)). *Mentha piperita* does not constitute a separate species, but is a hybrid of *Mentha viridis* and *Mentha aquatica*. It may be regarded as a sterile plant, as it fruits rarely, and even then the fruit is mostly badly-developed, hence the plant must be propagated by sub-dividing the rhizomes. Like all *Mentha*-species, *Mentha piperita* is extraordinarily variable. To add to the confusion, different varieties are cultivated in various plantations under the common denomination of “peppermint”. Several varieties also occur of the original species. *Mentha piperita* embraces two groups; group I including the subspecies *piperita*, Briq. with numerous varieties, while group II includes the sub-species *citrata*, Briq., which under the name of “citronelle” is much grown in France because of its pleasant aroma, but which does not appear to be used commercially. In its internal structure *Mentha piperita* exhibits certain features midway between those of *Mentha viridis* and *Mentha aquatica*. How variable are the *Mentha*-species is shown by *Mentha viridis*, L. and *Mentha aquatica*, L.; for the authors describe no fewer than six varieties of the former, and as many as eight of the latter, besides indicating many others.

As a complement to their botanical review the authors give the analytical peculiarities of the essential oils from the ordinary and from the

\(^1\) Berichte von Roure-Bertrand Fils, October 1911, 3.

<table>
<thead>
<tr>
<th></th>
<th>Ordinary Peppermint</th>
<th>Red Peppermint</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{150})</td>
<td>0,9191</td>
<td>0,9184</td>
</tr>
<tr>
<td>(\alpha_D)</td>
<td>(-10^\circ\ 54')</td>
<td>(-8^\circ\ 2')</td>
</tr>
<tr>
<td>Solubility in 80%/ alcohol</td>
<td>1 vol. afterwards clouding</td>
<td>–</td>
</tr>
<tr>
<td>Acid v.</td>
<td>0,8</td>
<td>0,8</td>
</tr>
<tr>
<td>Ester v.</td>
<td>40,5</td>
<td>31,7</td>
</tr>
<tr>
<td>Menthyl acetate</td>
<td>14,3%</td>
<td>11,2%</td>
</tr>
<tr>
<td>Ester v. after acet.</td>
<td>160,8</td>
<td>169,1</td>
</tr>
<tr>
<td>Total Menthol</td>
<td>50,9%</td>
<td>53,9%</td>
</tr>
<tr>
<td>Free Menthol</td>
<td>39,6%</td>
<td>45,1%</td>
</tr>
<tr>
<td>Proportion of Menthone</td>
<td>7,3%</td>
<td>–</td>
</tr>
</tbody>
</table>

\[\text{afterwards clouding}\]
so-called red peppermint. These are set forth in the table below. The red variety has only been cultivated in the South of France comparatively recently. It yields rather more oil (about 0,33%) than does the ordinary peppermint (about 0,25%), but its oil is not of so fine a quality as that of the last-named. Red peppermint will grow on soil where the ordinary variety can barely live. It may even be grown for five years in succession on the same land, while in the case of genuine peppermint it is necessary to interrupt the cultivation every third year.

**Peppermint Oil, Japanese.** We will abstain from correcting the statements relative to the probable yield of the crop which appeared in our last Report, because the news of the production in the various districts which has been received since then is again of such a contradictory character that the later figures would be of no greater value than those which have already been published. The only particular in which the reports agree is the admission that the result of the Hokkaido crop was considerably over-estimated last autumn. A large part of the crop is said to have been destroyed by floods, while another part has suffered to such an extent from the so-called “rust-worm” that it became necessary to cut the peppermint before it reached maturity, as a result of which there has been a serious loss of oil. This much, in any case, is certain, that all attempts to induce the Japanese to moderate their demands for oil and menthol have been fruitless, and remain so at the going to press of the present Report. Within the past few days, as a matter of fact, there has been a further decided increase in the quotations. Seeing that the demand in Europe is remarkably brisk and that several speculators will be compelled shortly to cover their bear-sales, we believe that considerably higher prices will rule within the next few months. A fairly long time still separates us from the new crop, and as it is our experience that the consumption, especially of menthol, has greatly increased of late, we regard it as highly probable that a decided scarcity will make itself felt in the course of the summer. Very much will depend, of course, upon the American peppermint-crop, of which the probable result, however, cannot be estimated for the present.

In the course of fractional distillation of a first runnings of Japanese peppermint oil we obtained a fraction giving b. p. 175 to 181°; $d_{15^0}$ 0,8436; $\alpha_D = 84^0 27'$; $n_{D30}$ 1,46773. It consisted chiefly of $l$-limonene, which was identified from its tetrabromide, m. p. 103,5 to 104,5°. As the fraction reacted faintly with sodium, we heated a small quantity with this metal. After distilling off the oil which had not been affected by the reaction and removing the unattacked sodium, we diluted the sodium-compound with

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2) On French peppermint oil also comp. Reports April 1905, 62; October 1906, 58; October 1907, 74; April 1909, 76; April 1911, 90.
water and distilled the resulting isolated oxygenous constituents with steam. A strong menthone odour still adhered to these constituents, which were treated with phthalic anhydride in order to isolate the alcoholic parts, the result being an acid phthalate which was readily soluble in the usual solvents. The crude product melted between 62 and 63°, the m. p. rising to between 64 and 65° after recrystallisation from benzene. Finally, when recrystallised from ether and chloroform, it gave m. p. 64,5 to 65,5°. The alcohol which was regenerated from the phthalate constituted an oil with an odour strongly reminding of secondary octyl alcohol: b. p. 57 to 58° (31/2 mm.), d150 0,8296, αD — 0°10', nD20 1,42652. When oxidised with bichromate of potassium and sulphuric acid the alcohol gave rise to a ketone of which the odour somewhat reminded of methylhexyl ketone. But it was evidently not this ketone, as was proved by the fact that it gave no reaction with neutralised sodium bisulphite solution. Moreover, the semicarbazon did not give the characteristic m. p. of methylhexyl ketone semicarbazone.

For the purpose of closer investigation we subjected a fraction possessing similar properties to that referred above to direct treatment with phthalic anhydride. The characters of this fraction were as follow: d150 0,8521, αD — 52°26', nD20 1,45991. The product which was recovered from the phthalate gave identical constants with the alcohol which was prepared from the previous fraction: b. p. 56° (31/2 mm.), d150 0,8279, αD ± 6°17', nD20 1,42775. These constants underwent scarcely any change as the result of distillation under ordinary pressure: b. p. 178,5 to 179,5°, d150 0,8276, αD ± 6°26', nD20 1,42755. Oxidation with sodium bichromate and sulphuric acid yielded a ketone which did not react with bisulphite. The product which was regenerated from the semicarbazone (m. p. 117°) possessed the following properties: b. p. 170°, d150 0,8255, αD + 0°22', nD20 1,41556. Apart from its low optical activity, which appears to be due to traces of impurity, the ketone possesses the constants of an ethyl-n-amyl ketone which was isolated by us some years ago from French lavender oil, and which were as follow: b. p. 169,5 to 170°, d150 0,8254, αD ± 0°, nD20 1,41536. A mixture of the semicarbazones of the two ketones suffered no depression of m. p. The above facts may be held to afford proof that the alcohol formed by us represents d-ethyl-n-amylcarbinol, CgH6CH(OH)C5H11.

We oxidised the alcohol with the calculated quantity sodium bichromate and sulphuric acid, and obtained capronic acid, proof being afforded by the b. p., the odour and analysis of the silver salt.

0,1543 g. substance: 0,0757 g. Ag.

<table>
<thead>
<tr>
<th>Found</th>
<th>Calc. for CgH11AgO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>49,06°/0</td>
</tr>
</tbody>
</table>

With phenylisocyanate no phenylurethane was formed; α-naphthyliso-
cyanate, on the other hand, gave rise to an α-naphthylurethane, m. p. 81 to 82° (from dil. methylalcohol).

We are at present engaged in preparing the alcohol synthetically, and in identifying it by preparing a few of the esters.

A new colour-reaction has been recommended for distinguishing Japanese peppermint oil from peppermint oils of other origin. We will content ourselves with placing the matter on record here because we only employ tests of this kind in exceptional cases, seeing that they lack all scientific foundation, and fail, moreover, in the case of mixtures. The author heats 1 cc. of the oil with 0.5 gram of a mixture of equal parts paraformaldehyde and citric acid over a water bath. With Japanese peppermint oil there is no decoloration, whereas with American, English, Italian (and as our tests show with Saxon oils also), a purple colour develops. This new test has the advantage of being quicker than the familiar colour reaction with concentrated acetic acid.


**Peppermint Oil, Russian.** A few years ago we reported on a peppermint oil which came from the Province of Tambov, in Central Russia. Recently, according to a statement by Maisit the cultivation of peppermint has also been taken up in the Caucasus, where the climate is more favourable, and where the plant is said to flourish so well that South Russian peppermint oil has been for some time a commercial article in the Russian home market. In the District of Sotshi, situated on the Black Sea, the black variety of English peppermint (*Mentha piperita*, Mitcham var. nigra), is chiefly cultivated. It is grown at an altitude of about 1500 feet and is distilled in newly-erected, modern distilling plant. According to the growers' statements the dried herb of the flowering plant yields from 1.6 to 1.7% of crude oil.

<table>
<thead>
<tr>
<th>Oil from</th>
<th>d_{20°}</th>
<th>α_{D}</th>
<th>Acid v.</th>
<th>Ester Menthol</th>
<th>Free Menthol</th>
<th>Total Menthol</th>
</tr>
</thead>
<tbody>
<tr>
<td>First year's plants</td>
<td>0.912</td>
<td>-17°42'</td>
<td>0.57</td>
<td>6.57%</td>
<td>42.44%</td>
<td>49.17%</td>
</tr>
<tr>
<td>Second year's plants</td>
<td>0.913</td>
<td>-17°57'</td>
<td>0.57</td>
<td>8.74%</td>
<td>41.33%</td>
<td>50.07%</td>
</tr>
</tbody>
</table>

Both oils were sparingly soluble in 70% alcohol, and when placed in a freezing mixture menthol began to separate out only after prolonged standing.

1) Perfum. and Essent. Oil Record 2 (1911), 275.
2) Report April 1907, 82.
3) Arch. der Pharm. 249 (1911), 637.
As will be seen from the table above, there are no remarkable differences in the constants of the oils. Maisit noticed that both oils, when distilled under ordinary pressure, left a remarkably high residue, about 18%. He ascribes this to the fact that both samples were crude distillates, but in our view the reason is more likely to have been that in the course of fractionation without reduction of pressure a partial decomposition of the oils took place.

**Oil of Persea pubescens (Pursh.), Sarg.** This laurel is a native of the central parts of North America and is commonly known as "swamp red bay" or simply as "swamp bay". According to Rabak, the leaves contain 0.2% of an oil possessing the following properties: $d_{850} 0.9272$, $\alpha_D + 22.4^\circ$, $n_{D25} 1.4695$, acid v. 2.8, ester v. 14.5, ester v. after acet. 64, sol. in $\frac{1}{8}$ vol. $80\%$ alcohol, the solution turning turbid when 5 vols. or more is added. Rabak detected in the oil only one free acid, viz., butyric acid; but it contained both butyric and valeric acids in the esterified state as well as slight proportions of oenanthic acid. Other constituents observed were: $21\% d$-camphor (m. p. of the semicarbazone 237 to 239°; m. p. of the oxime 117 to 118°), 19.8% cineole (m. p. of the hydrobromide 55 to 57°) and possibly small quantities of borneol and formaldehyde.

**Petitgrain Oil, Paraguay.** The pessimistic prognostications of our correspondents have unfortunately proved to be well-founded, and during the last few months it has been more difficult to procure fresh supplies than has perhaps been the case at any previous time. The revolution in Paraguay has adversely affected the industry, and to this obstacle has been added an inundation which has crippled the few distilling plants that had escaped the revolutionary disturbances. As a result the prices have risen, but it seems as if they had hardly yet reached their highest point, inasmuch as for the present there appears to be no prospect whatever of any improvement in the conditions. According to a report by the German Consulate of Asuncion, the exports of petitgrain oil in the year 1910 amounted to 28,056 kilos, which shows a falling-off of nearly 2000 kilos compared with 1909.

**Oil of Peucedanum Ostruthium.** F. Lange has recently investigated the oil of *Peucedanum Ostruthium*, Koch, the properties of which are as yet little known. The oil had been distilled from the dry roots of two year old plants grown in the Tyrol, the yield being 1% and the characters as follow: $d_{50} 0.8627$, $\alpha_{D50} + 59.30^\circ$, acid v. 0.8, sap. v. 17.9, ester v. after acet. 28.34. In addition to free palmitic acid the oil contained

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1) *P. carolinensis*, Nees of the Index Kewensis.
the following bodies in the esterified form: isobutyric acid, isovaleric acid, isopropylidene acetic acid (β, β-dimethylacrylic acid), formic acid and acetic acid. It is uncertain whether isopropylidene acetic acid was present in the original oil or whether it was only generated during the distilling process.

The oil contained 95% terpenes, among which the following were identified: dipentene (m. p. of the dihydrochloride 50°), d-limonene (m. p. of the nitrobenzylamine 92 to 93°), α-pinene (m. p. of the nitrobenzylamine 122 to 123°) d-phellandrene (m. p. of the nitrite 103 to 104°). The oil also contained an alcohol C_{16}H_{20}O (?), of which the phenylurethane melted at 145 to 146°. Finally, Lange detected the presence in the oil of a sesqui-terpene, which yielded a dihydrochloride melting at 157 to 157.5°.

Angelicaldehyde, which is mentioned by Wagner as a constituent of the oil, was not found in it by Lange.

**Pimento Oil.** It has been necessary to raise the price in the course of the winter, because the arrivals of pimento of a quality suitable for distilling have been very scanty and raw material has commanded higher rates. For the present there does not seem to be any prospect of a reduction, as the demand is much in excess of the production.

**Pine-needle Oils.** The principal interest continues to be centred upon Siberian pine-needle oil, because that variety occupies a specially favoured place among the oils which are adapted for all kinds of technical purposes and at the same time possesses the advantage of cheapness. The aroma of this oil is so pleasant and powerful that it has also secured for the article an opening in numerous manufactures which formerly relied exclusively upon the more costly varieties of pine-needle oils. Pine-needle oil from *Abies pectinata*, and oil from the cones (*O. templinum*), were in plentiful supply; on the other hand the distillation of oil from *Pinus Pumilio* is being restricted in some of the producing districts, because this manufacture no longer pays at the present depressed selling-prices, and because it is becoming a more and more difficult and costly matter to procure the raw material for distilling. For the present it is impossible to say in how far this fact will influence the course of prices in the near future.

We seize this opportunity to point out once more that for many years past oils have been placed upon the market from various districts, which, although of quite excellent quality, possess a rather lower specific gravity and a higher optical rotation than are ordinarily considered admissible in oil of *Pinus pumilio*. We have already called attention to this matter in a previous Report (October 1906, 62), and we will now only add the supplementary statement that it is absolutely necessary to recognise the existence of these deviations from the normal, as other oils are at times unprocurable.
The same observation applies to the slight differences in odour which are observable in pumilio oil, and which occasionally lead to complaints by customers that a certain parcel of oil supplied to them does not possess a sufficiently fine aroma. In the case of an article such as pumilio oil, which is being distilled all through the year, small deviations in scent are quite unavoidable, for it is obvious that differences in the degree of maturity of the material worked up will make themselves felt in the odour of the oil also, which therefore varies according to the season when the oil was distilled. The difference is not important, but it is of course noticeable by the expert. It is quite impossible to guarantee to supply pumilio oil of which the scent will always be the same.

Oil of Pluchea foetida. The green herb of *Pluchea foetida*, D. C. (*P. camphorata*, D. C. of the Index Kewensis), N. O. Compositæ, yields according to F. Rabak\(^1\) 0,025% of a pale golden-yellow essential oil: d \(0,9329\), \(\alpha_D - 5,4^\circ\) (in a 50 mm. tube), \(n_{D250} 1,4845\), acid v. 4,1, ester v. 44, sap. v. after acet. 104. It is soluble in its own volume of 80% alcohol, the solution turning cloudy upon the addition of 5 vols. a. m. Cineole (m. p. of the iodol-compound 113\(^{\circ}\)) was found to be a constituent of the oil.

Oil of Ramona stachyoides. *Ramona stachyoides* (Benth.), Briquet, (*Audibertia stachyoides*, Benth.; *Salvia mellifera*, Greene) is a shrub-like labiate which occurs in Southern California and is there known as "black sage". The green flowering plant, distilled by Rabak\(^2\), yielded 0,75% of a colourless oil with a camphoraceous odour, possessing the following properties: d \(0,9144\), \(\alpha_D + 30,2^\circ\), \(n_{D250} 1,4682\), acid v. 2, ester v. 2,5, ester v. after acet. 27,1, sol. in 1,5 vols. 70% alcohol, the solution turning turbid when more than 3,5 vols. is added. At \(-15^\circ\) 11,3% \(d\)-camphor (m. p. 174 to 175\(^{\circ}\); m. p. of the semicarbazone 232 to 233\(^{\circ}\)) is separated out from the oil. Rabak's sample contained small quantities of formic acid in the free state, while acetic acid and possibly traces of formic acid were present in combination. The oil also contains about 22,5% cineole (m. p. of the iodol compound 111 to 112\(^{\circ}\)) and possibly pinene, thujone and borneol. Its total camphor-content is about 40%.

Rasama Oil. Rasama oil\(^3\), a volatile oil, has been found at Buitenzorg\(^1\) to possess the following constants: d \(0,924\), \(\alpha_D - 51^\circ 24'\). The principal part of the oil appears to consist of sesquiterpenes: b. p. 250 to 258\(^{\circ}\).

Rose Oil, Bulgarian. The Bulgarian rose oil market has during recent months been under the influence of a pronounced lack of business, and although certain wealthy firms have tried with great pertinacity to

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1) Midland Drugg. and pharm. Review 45 (1911), 485.
3) The original reference contains no particulars of the parent-plant.
4) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 50.
maintain the price at about 2000 francs per kilo (the figure which it had reached in September 1911), they were nevertheless compelled, as time went on, to show a more tractable spirit in order not to be left with their stocks on hand. As no orders of any magnitude came forward, prices finally receded to about 1700 francs per kilo. At that level, however, they have remained steady, because in the meantime news has been received from the growing districts, announcing that the plantations have been seriously damaged by the severe winter, and that the prospects of the new crop have again become unfavourable. In any case, however, it is still too soon to express a reliable opinion on the probable development of the flowers. The weather during the months of April and May will be the chief determining factor in this respect.

In Gildemeister and Hoffmann's book The Volatile Oils (p. 429) the maximum limit of value of the optical rotation of rose oil is stated to be \(\alpha_D - 4^\circ\). Afterwards we reduced this limit to \(-3^\circ\). Later, in our Report of October 1910 (p. 111), we called attention to the fact that Parry had examined six samples of rose oils alleged to be pure, of which the optical rotation ranged from \(-4^\circ\) to \(-5^\circ\), whereas in our own experience we had only once encountered a sample with \(\alpha_D - 4^\circ 20'\). More recently, a few instances have again occurred in which Bulgarian rose oils, when examined in our laboratory, have shown an optical rotation exceeding \(-4^\circ\), their constants in other respects being normal. Quite lately another such oil came under our notice. Its constants were: \(d_{400} 0,8608\), \(\alpha_D - 4^\circ 32'\), \(n_{D50} 1,46565\), sol. p. \(+19^\circ\), acid v. 1,5, ester v. 9,5, total geraniol 68,3%o. When the oil was washed out with water its specific gravity remained unaltered, but the co-efficient of refraction had risen to 1,46704, a value which had never before come under our notice in rose oil of good quality (compare Report April 1910, 93).

Our suspicion that the sample under examination represented an adulterated article was confirmed by the striking discovery that the stearoptene which had separated out from the oil was semi-liquid at ordinary temperature and rotated strongly, whereas the stearoptene of rose oil of normal condition is at most feebly active, and is solid at room-temperature. It was therefore evident that a liquid material possessing strong optical rotatory power had been added to the oil. Upon further examination of the oily constituents, which in each case had again been freed from solid paraffin by freezing, we obtained, among other fractions, one which possessed the following physical characteristics: b. p. 95 to 96° (4 mm.), 255 to 260° (756 mm.), \(d_{150} 0,9203\), \(\alpha_D - 63^\circ 55'\), \(n_{D50} 1,49975\).

After being saturated with hydrochloric acid gas in an absolute ethereal solution the oil afforded no solid hydrochloride even when left to stand

1) Report October 1904, 81.
for several days. Combustion showed the fraction to consist of a hydrocarbon $C_{18}H_{34}$, only slightly contaminated by oxygenous constituents.

$$0.4062 \text{ g. substance: } 1.2836 \text{ g. } \text{CO}_2, \ 0.4194 \text{ g. } \text{H}_2\text{O}.$$  

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<th>Found</th>
<th>Calc. for</th>
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<td>C 86.18%</td>
<td>88.23%</td>
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<tr>
<td>H 11.48%</td>
<td>11.77%</td>
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For purposes of further purification the hydrocarbon was treated with metallic sodium and resolved into separate fractions. By this method we finally isolated an oil possessing the following constants: b. p. 95,5° (4 mm.), 258 to 261° (756 mm.), $d_{15}^0 0.9206$, $\alpha_p - 81° 56'$, $n_{D30}^0 1.50049$.

The fraction was treated for obtaining nitrosate and nitrosochloride, but without positive result. The strong lÆvorotation of all these fractions appeared to indicate that they might consist of gurjun balsam oil. Now it is well-known that some time ago Deussen and Philipp¹, by oxidising gurjun balsam oil with permanganate in acetone solution, obtained a reaction-product which, it appears, may serve as a criterion for the detection of the addition of gurjun balsam oil to other oils, a view which is borne out by our present experience. The oxidation-product, b. p. 175 to 178° (12 mm.), is according to Deussen a ketone, and is sharply characterised by a semicarbazone melting at 234° and rather sparingly soluble in alcohol. The fractions of our sample with the strongest rotatory power had already been used up for other reactions, and for the purpose of oxidation only the two following fractions, amounting in all to about 14 g., were left:

1. B. p. 255 to 260°, $\alpha_p - 50° 32'$
2. B. p. 260 to 262°, $\alpha_p - 48° 53'$

The oil was dissolved in about 200 g. acetone, diluted with 35 g. water, and to the clear solution were gradually added 15 g. solid powdered permanganate. The unattacked oil, which boiled at 104 to 105° (5 mm.) was removed by fractionation and the distillation-residue treated with semicarbazide. The reaction-product was left standing overnight, when, after the addition of water, it was deposited as an oily precipitate, solidifying in part after prolonged cooling in ice under stirring with alcohol. The semicarbazone, repeatedly recrystallised from hot alcohol, had m. p. 234°, and, with a semicarbazone of the same m. p. and constants, prepared from gurjun balsam oil for purposes of comparison, suffered no depression of m. p. These two bodies were therefore identical.

From the result of the above examination it is to be concluded that the strongly lÆvorotatory oil which had been added to the stearoptene of the rose oil consisted principally of gurjun balsam oil, which had been improperly added to the rose oil for purposes of adulteration. Possibly

an adulterant previously observed by Parry\textsuperscript{1}), which possessed a high rotatory power may also have been gurjun balsam oil, or a mixture of that oil with some other substance, for Parry states that this addition had also raised the alcohol-content of the oils. It will therefore be advisable to keep this adulteration in view for the future. In the isolation of the rose-oil stearoptene, gurjun balsam oil is precipitated together with the stearoptene, and it may therefore be desirable to extend the examination of rose oils in this direction and to submit the stearoptenes to closer examination, at any rate in all cases in which the rotation of the oil in question exceeds $-2^\circ 30'$.

We may quote particulars of two other samples of rose oils which have been examined in our laboratory in the course of the past few months. The first represented a rose oil which had been offered to us for pur-

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<th>No. 1</th>
<th>No. 2</th>
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<tr>
<td></td>
<td>Original oil</td>
<td>Extracted with water</td>
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</tr>
<tr>
<td>$d_{80^o}$</td>
<td>0,8755</td>
<td>0,8793</td>
</tr>
<tr>
<td>$n_{D25^o}$</td>
<td>$-20^\circ 36'$</td>
<td>$-21^\circ 50'$</td>
</tr>
<tr>
<td>Sol. p.</td>
<td>$+10,7^\circ$</td>
<td>$+18,0^\circ$</td>
</tr>
<tr>
<td>Acid v.</td>
<td>1,0</td>
<td>1,8</td>
</tr>
<tr>
<td>Ester v.</td>
<td>7,6</td>
<td>19,1</td>
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<tr>
<td>Ester v. after acet.</td>
<td>119,9</td>
<td>249,7</td>
</tr>
<tr>
<td>Total geraniol.</td>
<td>36,2%</td>
<td>84,5%</td>
</tr>
<tr>
<td>Quantity of added alcohol\textsuperscript{2})</td>
<td>6,5%</td>
<td>6%</td>
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chase, and which every analyst, even upon cursory examination, would have rejected as highly adulterated on account of the great abnormity of its constants. Apart from the alcohol which we discovered to be present in it (see the table below), it is possible that this oil was also adulterated with gurjun balsam oil, but the sample at our disposal was unfortunately too small to permit of its examination for this adulterant.

The second sample submitted to us for our opinion had already been examined in another quarter and, singularly enough, had been pronounced to be unobjectionable, notwithstanding that a carefully executed control-test made by us easily showed it to be also adulterated. (For the method of testing compare Reports November 1908, 107, and April 1910, 93.) This sample contained in the first place about 6\% spirit, calculated for 90\% alcohol. In the next place, the specific gravity and coefficient of refraction of the

\textsuperscript{1} Chemist and Druggist 77 (1910), 261; Report October 1910, 111.

\textsuperscript{2} The alcohol was isolated as such.
de-alcoholised oil were outside the limits of value of rose oil, and furthermore the total-geraniol content (even after removal of the alcohol, which would have been converted by acetylation into acetic ester, and as such would likewise have raised the saponification value of the acetylated oil) was considerably too high, from which it was to be inferred that either palmarosa oil or geraniol had been added to the sample in addition to the other adulterants.

**Rose Oil, German.** The exceptionally cold weather of last winter, during which the thermometer on occasions fell to $-22\degree C$, has been well-supported by our rose-plantations, and unless, as was the case last year, there should be night-frosts in May or June, the prospects of our Miltitz rose-crop for the present year may be described as very bright indeed. At present it remains doubtful, however, whether, in spite of the extension of our plantations last autumn, we shall collect sufficient raw material to enable us again to take up the distillation of oil. The manufacture of our new speciality "Red Rose Schimmel & Co." (see p. 147), which has the natural flower as its basis, and of which the peculiar properties place it in the front-rank of all rose-products, requires such large quantities of newly-gathered roses, to make us fear that the whole of our output will be taken up by this branch of our works.

**Rosemary Oil.** The position of the rosemary oil industry in the South of France is by no means bright, for the fact must be plainly admitted that the monopoly of quality, which was formerly in the hands of the French, now appears to be a thing of the past. Although, speaking generally, the distillation of such oils in Spain is not conducted with particular care, that country has recently been placing upon the market ever-growing quantities of oil which is in no respect distinguishable from the French distillate. The prices of the Spanish oil are considerably lower than those of the French, and as the distillers in Southern France have been complaining for years that there was no profit in the article, it would appear as if the days of the Southern French rosemary oil industry were numbered. In sympathy with the slight demand for Dalmatian rose oil the producers of that article have somewhat lowered their pretensions of late. Just recently there are reports that the coming crop will be a failure, but in view of the lessened demand we doubt, for the present, whether these reports will greatly affect the prices.

**Samphire Oil.** The distribution of the essential oil in the leaves, stems and flower-parts of samphire (*Crithmum maritimum*, L., N. O. Umbelliferae) has been described by L. Francesconi and E. Sernagiotto$^1$.

**Sandalwood Oil, East Indian.** Our anticipations of the probable course of the sandalwood prices have been amply confirmed: throughout the winter the tendency was very firm, and for the important sales which

$^1$ Rendiconti della R. Accademia dei Lincei (5), 20, II. (1911), 249.
have been effected the buyers have been compelled to pay higher rates. A glance at the comparative tables on pages 114 and 115 of this Report, showing the prices realized at the two series of auctions in 1911 and 1910, will be sufficient to convince the reader that the oil-quotations are fully warranted, and if account be taken of the probability that all the cheap lots held over from former years have been worked up in the meantime, and that the demand is growing from year to year, it will be hard to discover any logical reasons for a decline in prices.

How irksome the sandalwood oil business must have become for a few competing firms, especially abroad, is most clearly seen from the fact that from time to time these firms attempt to sell off some part of their output far below the current price, merely in order to avoid having the oil (which generally bears evidence of having been distilled in the most primitive way) left on their hands. Offers of this kind recur periodically, but they remain without the slightest effect upon the market, because, of course, the standard of price is set only by a perfect distillate containing 94% santalol, such as is supplied by us. We have already fully described the size and importance of our sandalwood oil department in a previous Report. All through the winter our plant has been working day and night, yet we have been unable to accumulate stock, which surely proves in the most striking manner possible that the superiority of our distillate is appropriately acknowledged by the consumers. According to the reports at present available the future of the article can only be described as very firm, and we think that we may with a clear conscience advise our friends to choose the present moment for covering their requirements.

There is, we think, little doubt that as soon as the wood from last autumn's auctions is brought to the stills a further advance in the price of oil will be unavoidable. The complaints by capsule-manufacturers of depression of the prices of their product by extreme competition still persist, and we strongly recommend our numerous customers in this branch of industry to remember that the services of our research-laboratory are gratuitously at their disposal whenever they are faced with competition at prices which seem to indicate that the article thus offered is adulterated. We are quite prepared to allow our friends to make what use they please of our expert-opinion, if need be even in a court of law. Possibly this repeated reminder may in a few instances help to put a check upon the malpractices.

We have recently had occasion to examine an East Indian sandalwood oil taken from the capsules which had been sent to us for our opinion, and found it to possess the following characters: $d_{150} 0.9688, \alpha_p - 19^\circ 30'$, ester v. after acet. 152.3, equal to 67.6% santalol, insoluble in 70% alcohol. In this case it was obvious that there had been adulteration with cedarwood oil, inasmuch as, with a normal rotation, the sp. gr. was much too low, and the solubility so imperfect that the oil was altogether insoluble
in 70\%/ alcohol. From the low santalol content it may be inferred that the adulterant constituted about one-third of the oil.

From a note in *The Chemist and Druggist* [79 (1911), 612] we also gather that in the adulteration of oil sold in the form of capsules the residues of santalol manufacture are being used as well as West Indian sandalwood oil. The principal market for capsules thus adulterated is said to be Australia, where the capsules are sold at prices barely covering the cost of the oil. Several samples recently examined had the following characters: d\textsubscript{150} 0,962 to 0,966, \( \alpha_d + 8^\circ \) to \(-4^\circ \), insoluble in 10 vols. 70\%/ alcohol.

**Sandalwood Oil, West Indian.** In this article also there has been no excessive accumulation of stocks during the past few months. It is true that heavy consignments of wood have reached us regularly, but the demand has kept a fairly equal pace with the production, while large orders from the United States kept the deliveries at a steady level. At present the prospects remain unchanged, but there have lately been many rumours of difficulties in transport in Venezuela, and it is possible that ultimately, as a result of such difficulties, the wood may become dearer.

**Santolina Oil.** This oil, which was described in our last Report (p. 108), has already been examined in the same year by L. Francesconi and P. Scaraffia\(^1\)). The authors, by using the reagents which they had already employed on previous occasions, viz., osmic acid, ferric chloride solution and dilute alcoholic "Soudan-III" solution (see p. 31), discovered the essential oil to be principally located in the epidermic tissues. The yield varied from 0,198 to 1,15\%/ according to the stage of development of the plant, being highest shortly before the flowering. The constitution of the oil likewise varies according to the period of maturity of the plant. The average constitution of the oil was C 81,68\%/ H 11,28\%/ O 7,04\%/ and its average constants as follow: \( d_{150} 0,8732, [\alpha]_{D25} -11,74^\circ \). The first fractions contained a terpene (b. p. 165 to 170\(^\circ\)) and probably a phenol ether. With hydroxylamine hydrochloride the oil yielded an oxime and a hydroxylamine oxime. The corresponding ketone, which Francesconi and Scaraffia call santolinone, they regard as \( \Delta^{1(\gamma)} \)-menthene-2-one. The hydroxylamine oxime melts at 190\(^\circ\) with previous softening at 180 to 185\(^\circ\).

\[ \begin{align*}
\text{C:CH}_2 \\
\text{H}_2\text{C} & \quad \text{CO} \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{CH} & \quad \text{CH(\text{CH}_3)_2} \\
\text{C:CH}_2 & \quad \text{CH:CH}_2 \cdot \text{NH(OH)} \\
\text{H}_2\text{C} & \quad \text{C:NOH} \\
\text{H}_2\text{C} & \quad \text{CH}_2 \\
\text{CH} & \quad \text{CH(\text{CH}_3)_2} \\
\Delta^{1(\gamma)} \text{-Menthene-2-one.} & \quad \text{Hydroxylamine oxime.}
\end{align*} \]

## Sandalwood auctions 1911.

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<tr>
<th>Description</th>
<th>Tirthahalli Nov. 13</th>
<th>Tirthahalli Nov. 16</th>
<th>Tirthahalli Nov. 20</th>
<th>Sagar Nov. 23</th>
<th>Sagar Nov. 27</th>
<th>Shimoga Nov. 23</th>
<th>Chikmagalur Nov. 27</th>
<th>Hassan Nov. 30</th>
<th>Bangalore Dec. 4</th>
<th>Bangalore Dec. 13</th>
<th>Seringapatam Dec. 16</th>
<th>Hunsur Dec. 18</th>
<th>Fraserpett Dec. 18</th>
<th>Total Tons</th>
<th>Total Cwts.</th>
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<tr>
<td>1st Class Billets</td>
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<td>200</td>
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<td>121</td>
<td>12(\frac{3}{4})</td>
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* Last season's wood.
Comparative prices obtained at the sandalwood auctions of 1910 and 1911.

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<th>Prices realized</th>
<th>Tirthahalli 17/12</th>
<th>Sagar 14/12 1910</th>
<th>Shimoga 16/11 1910</th>
<th>Tarikere 8/12 1910</th>
<th>Chikmagalur 5/12 1910</th>
<th>Hassan 1/12 1910</th>
<th>Bangalore 28/11 1910</th>
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<td>46/9</td>
<td>45/3</td>
<td>48/3</td>
<td>46/6</td>
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<td>45/9</td>
<td>42/6</td>
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<td>46/6</td>
<td>43/6</td>
<td>47/6</td>
<td>49/-</td>
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<td>49/-</td>
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<td>43/3</td>
<td>49/-</td>
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<td>49/-</td>
<td>42/6</td>
<td>49/6</td>
<td>42/-</td>
<td>50/3</td>
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<td>2nd &quot; &quot;</td>
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<td>40/3</td>
<td>48/3</td>
<td>40/9</td>
<td>48/3</td>
<td>41/3</td>
<td>49/-</td>
<td>49/6</td>
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<td>39/-</td>
<td>51/-</td>
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<td>A in Bagar</td>
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<td>CHERIA</td>
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<td>A in Chilta</td>
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<td>28/6</td>
<td>29/6</td>
<td>30/9</td>
<td>33/6</td>
<td>34/9</td>
<td>32/-</td>
<td>31/-</td>
<td>34/6</td>
<td>36/-</td>
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<td>Hatri Chilta</td>
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<tr>
<td>Milwa Chilta</td>
<td>25/3</td>
<td>26/3</td>
<td>25/-</td>
<td>25/-</td>
<td>24/3</td>
<td>27/6</td>
<td>25/6</td>
<td>26/3</td>
<td>24/6</td>
<td>28/6</td>
</tr>
<tr>
<td>Basola Bukni</td>
<td>21/-</td>
<td>18/6</td>
<td>19/3</td>
<td>21/-</td>
<td>23/-</td>
<td>21/6</td>
<td>18/6</td>
<td>22/6</td>
<td>19/6</td>
<td>23/6</td>
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</table>
**Sassafras Oil.** There has been no alteration in the value of this oil. In view of the abundant supplies which came forward during autumn and winter, present quotations are likely to remain unchanged, the eager demand preventing a decline of prices.

**Satureja Oil.** An oil which is perhaps derived from *Satureja montana*, and which resembles in its properties the oil of *Satureja cuneifolia* which has been examined by us\(^1\), is described by S. S. Pickles\(^3\). The dry herb, which came from Trieste, yielded 1,64% oil with an odour resembling that of carvacrol, and possessing the following constants: \(d_{150}^0 0,9548\), \(\alpha_D 1°3'\), sol. in 2,7 vols. 70% alcohol. The oil contained 68,75% phenols, chiefly consisting of carvacrol.

Two distillates from the flowering herb of *Satureja montana* which were prepared by ourselves in the South of France some little time ago, may be included in the present reference. The oils were respectively of a lemon-yellow and a brownish colour; their odour reminded of thyme. Their characters were as follow:

<table>
<thead>
<tr>
<th></th>
<th>Yield</th>
<th>(d_{150}^0)</th>
<th>(\alpha_D)</th>
<th>(n_{D200})</th>
<th>Sol. in 8 vol. a m.</th>
<th>Sol. in 1,5 vol. a m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled at Barrême</td>
<td>0,23(^o)%</td>
<td>0,908</td>
<td>— 1°42'</td>
<td>1,49488</td>
<td>80% alcohol</td>
<td>80% alcohol</td>
</tr>
<tr>
<td>Distilled at Sault</td>
<td>0,15(^o)%</td>
<td>0,9194</td>
<td>— 4°48'</td>
<td>—</td>
<td>—</td>
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</tbody>
</table>

Both oils contained carvacrol, this body being represented in the Barrême oil by about 27% and in that from Sault by about 32%. We may add that *Satureja montana* is popularly known in the French Alps as “poivre d’âne”.

**Oil of Seseli Bocconi.** L. Francesconi and E. Sernagiotto\(^4\) have distilled from *Seseli Bocconi*, Guss. (*Bubon siculus*, Spr.; *Crithmum siculum*, Boccon; N. O. Umbelliferae) 0,295% of an essential oil with sp. gr. 0,8475 (27°). Closer examination of the oil showed that \(l\)-pinene and \(\beta\)-phellandrene are to be regarded as its principal constituents. On a previous occasion the authors had described the distribution of the oil in the leaves, flower-stalks and stems of the plant\(^4\). The root contains but little oil.

**Shaddock (Grape fruit) Leaf Oil.** There appear to be two varieties of the shaddock-tree (*Citrus decumana*, L.), a large-leaved shaddock, which is almost devoid of oil-cells, and a small-leaved variety. From the latter

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2) Proceed. chem. Soc. 27 (1911), 285. See also Bull. Imp. Inst. 9 (1911), 388.
4) Atti R. Accad. dei Lincei, Roma (5), 20, II. (1911), 249. From a reprint kindly sent to us.
Brooks') has obtained by distillation 1.7% of an oil with an agreeable aroma, possessing the following properties: $d_{25}^{20} 0.8700, \alpha_{D25} 22.90^o (+?)$, $n_{D25} 1.4644$, ester v. 10, sol. in 70% alcohol. The oil contains 25% di-pentene (m. p. of the tetrabromide 120°), 15% linalool (identified from its b. p. and from oxidation into citral) and 1% of an aldehyde reacting with bisulphite and possessing an odour of citral.

**Spearmint Oil.** The advancing tendency which has characterised this article since our last Report, and which still marks it, is chiefly traceable to the fact that the result of last autumn's distilling has brought universal disappointment, the expected yield not having been reached by a very long way. A few important producers have been compelled to purchase the annulment of their contracts for delivery. The demand was especially brisk in the United States, where, as is well known, spearmint oil is principally used for flavouring chewing gum. Our New York friends forecast unchanged high prices until the summer arrives, when a fall is not impossible, inasmuch as the high prices have induced many Western planters to extend their plantations considerably.

A spearmint oil of which the sample proved to be highly adulterated was recently offered to us from Russia.

Very interesting is the chemical examination of an authentic sample of American spearmint oil which has been carried out by E. K. Nelson. The oil, which has been distilled in Michigan from selected raw material, possessed the following characters: $d_{25}^{20} 0.9290, \alpha_{D25} 52.16^o, n_{D25} 1.4866$, ester v. 12.4, ester v. after acet. 36.4, sol. in its own vol. 80% alcohol. It contained about 66% carvone. After eliminating the carvone, Nelson ascertained the presence in the oil of phellandrene (identified from the nitrosite) as well as of l-limonene, which he identified by conversion into the nitrosochloride and into carvoxime.

Some time ago Elze had discovered dihydrocuminic acetate to be the carrier of the odorous principle of German spearmint oil. Singularly enough this ester was not present in the authentic American oil, which, however, contained the acetate of dihydrocarveol, an alcohol of which we had detected the presence in caraway oil several years ago. Nelson isolated dihydrocarveol from a fraction of the saponified oil which boiled between 100 and 115° (10 mm.). The alcohol reacted imperfectly with phthalic anhydride; it was found easier to separate it by heating to 125° with succinic anhydride. The dihydrocarveol was identified from its constants as well as by oxidising it into dihydrocarvone (m. p. of the semi-

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1) Philippine Journ. of Sc. 6, A. (1911), 349.
carbazone 200 to 201° when heating rapidly; m. p. of the oxime 88 to 89°. The acetic ester of dihydrocarveol had an odour of spearmint.

In addition to acetic acid and possibly also butyric, caproic or caprylic acids, the oil contained 0,1°/o of a solid acid, m. p. 182 to 184° which has also been observed by Nelson in several other samples of spearmint oil.

No fraction of the oil under examination had an odour of menthol.

According to K. Irk1), Hungarian spearmint oil constitutes a straw-coloured or faintly greenish-yellow liquid: \(d_{40}^{18} = 0,9375\) to 0,9513, \(\alpha_D = 44,38\) to 49,85°, \(n_{Dro} = 1,4899\) to 1,4931, soluble in its own vol. of 80°/o and in one-half its own vol. and more of 90°/o alcohol. It contains from 62 to 71°/o \(l\)-carvone. The green herb yields 0,5278°/o, and the dry herb from 1,8530 to 2,4814°/o oil.

We have already previously reported on Hungarian spearmint oil (comp. Report April 1909, 85).

**Spike Oil.** At the commencement of March we found it necessary again to raise our prices, as the stocks of our excellent pure spike oil were approaching depletion and cannot be renewed before next August or September. We are therefore unable to execute large orders unless a suitable time for delivery is granted.

In our Report of November 1908, 115 we stated that spike oils of really good quality should be soluble in about 15 to 20 times their volume of 60°/o alcohol, if distilled by the method customary in France (à feu nu). Since then we have been privately informed that it has been observed that the degree of solubility of spike oil varies according to the origin of the oil. Oils from the Alps and from Provence are said to be soluble in 60°/o alcohol, and oils from the neighbourhood of Roche-Esclapon, a village in the Var, are said to dissolve even in 58°/o alcohol. On the other hand, the distillates from the Departments of the Bouches-du-Rhône, Vaucluse, Gard, Hérault and Aude, are said to be only rarely soluble in 60°/o alcohol. The differences are said to be due to variations in the conditions of the soil and the climate, and also to the method of distilling, distillation being often carried out without water and cooling. The matter is further complicated by the circumstance that, in order to increase the weight, the herb-cutters often mix with the spike other plants, such as *Satureja montana*, L., *Calamintha officinalis*, Moench, *Sideritis romana*, L., *Teucrium Polium*, L., &c., which, when the admixture is moderate, it is very difficult to pick out. With the object of checking the accuracy of these

1) Kiserletügyi Közlemények 14 (1911). From a reprint kindly sent to us. Also see Pharm. Zentralh. 82 (1911), 1111.
statements we caused a business-friend to make for us a collection of spike oils from various Departments. In the result we were unable to confirm the assertion that the degree of solubility depends upon the origin of the oil. On the contrary, our experience, as shown in the table printed below, is that generally speaking all the oils are soluble in the same degree, and that deviations occur independently of the locality of production. From this it may perhaps be inferred that the differences in solubility are actually determined only by the different methods of distillation or by the greater or less degree of care bestowed upon the collection of the raw material.

<table>
<thead>
<tr>
<th>Origin</th>
<th>d₁₀₀</th>
<th>α₀</th>
<th>α₀ of the initial 10%</th>
<th>acid v.</th>
<th>ester v.</th>
<th>Solubility in 60% alcohol</th>
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<tr>
<td>La Palud de Moustiers</td>
<td>0,9040</td>
<td>-2° 12'</td>
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<td>0,9052</td>
<td>-1° 47'</td>
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<td>9,0</td>
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<td>Les Méés</td>
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<td>+0° 15'</td>
<td>+3° 30'</td>
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<td>in 6 vols. a.m.</td>
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<td>Forcalquier</td>
<td>0,9071</td>
<td>+0° 24'</td>
<td>+4° 0'</td>
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<td>14,1</td>
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<td>-0° 28'</td>
<td>+2° 34'</td>
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<td>9,4</td>
<td>in 7 vols. a.m.</td>
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<td>Pertuis</td>
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<td>6,9</td>
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<td>+3° 38'</td>
<td>+5° 26'</td>
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<td>7,5</td>
<td>in 14 vols. a.m.</td>
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</table>

**Star Anise Oil.** Since our last Report a change of importance has occurred in the position of the article, the primary cause of which was to be found in large sales of both Chinese and Tonquin oil, as a result of which the prices rapidly advanced by about 10 per cent. Next, the outbreak of the Chinese revolution afforded a further reason for giving a firm tendency to the market and, finally, when owing to the unsettlement of the political conditions the supplies from the interior were cut off, the quotations advanced to about 6/-. Some of the shippers in these circumstances pleaded *force majeure*, but opinions varied as to the justification of this plea. In any case, during the past few weeks the market has calmed down to this extent that offers are once more available. It is natural that for the present the quotations should still remain very high and it will depend upon the demand whether a further advance will occur. At the present high figures there have not, so far as we know, been any transactions of importance. From the other side the position is described as firm.
E. W. Mann\(^1\) attributes the imperfect solubility of certain star anise oils in 90\(\%\) alcohol to some form of sophistication the true nature of which has been unable to determine; but which he surmises to have its source in cedar wood oil, because the distillation residues of the samples examined by him possessed a well-marked woody flavour not dissimilar to that of cedar wood oil, which was not perceptible in the residue of an oil of normal solubility. In our opinion any addition of this character can only have been a slight one, because cedar wood oil is somewhat strongly laevorotatory, and Mann’s samples only showed rotations ranging from ±0° to a maximum of —0°12’. A sophistication of the kind suggested appears to us to be all the more doubtful, because we ourselves some years ago, and again recently, have observed readily-soluble star anise oils, but these were found to be adulterated with fatty oil, which was isolated by driving off the volatile fractions with steam, and was clearly identified by its insolubility in 95\(\%\) alcohol, its high saponification value and the melting-point of the isolated fatty acids. The subjoined table shows the characteristics of our oils, both before and after rectification by steam, and of the distillation residues:

<table>
<thead>
<tr>
<th></th>
<th>(d_{20}^°)</th>
<th>(\alpha_0)</th>
<th>Sol. pt.</th>
<th>Sol. in 90(%) alcohol</th>
<th>Sap. v.</th>
<th>m. p. of the fatty acids</th>
</tr>
</thead>
<tbody>
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<td>Original Oils</td>
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<tr>
<td>1) 0,9807</td>
<td>— 0° 15’</td>
<td>+ 15,8°</td>
<td></td>
<td>Both insol. in 10 vols.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2) 0,9800</td>
<td>— 0° 9’</td>
<td>+ 15,5°</td>
<td></td>
<td></td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>The same</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rectified</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) 0,9805</td>
<td>— 0° 15’</td>
<td>+ 16,1°</td>
<td></td>
<td>in 2 vols. a. m.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2) 0,9816</td>
<td>— 0° 11’</td>
<td>+ 16°</td>
<td></td>
<td>in 3 vols. a. m.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Dist. residue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) —</td>
<td>—</td>
<td>—</td>
<td></td>
<td>Both insol. in 10 vols.</td>
<td>140,1</td>
<td>29 to 30°</td>
</tr>
<tr>
<td>2) —</td>
<td>—</td>
<td>—</td>
<td></td>
<td>95% alcohol</td>
<td>148,0</td>
<td>39°</td>
</tr>
</tbody>
</table>

**Tansy Oil** has also advanced in price. It is probable that there will be a further rise in the quotations, as there is only a little oil left over from the last crop.

**Oil of Thuja plicata.** From the leaves and branches of the Washington cedar (*Thuja plicata*, Lamb.), R. E. Rose and C. Livingstone\(^2\) have obtained by distillation 1\(\%\) of a pale yellow oil of the following characters: \(d_{20}^°\) 0,913, \([\alpha]_{D20}^°\) — 4,77°, \(n_{D20}^°\) 1,4552, acid v. 0,518, ester v. 2,28, ester v. after acet. 8,8. The oil was soluble in any proportion in 70\(\%\) alcohol; 85\(\%\) of the oil distilled between 100 and 110° (40 mm.) and consisted of

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\(^1\) Perfum. and Essent. Oil Record 2 (1911), 273.

\(^2\) Journ. Americ. chem. Soc. 34 (1912), 201.
\(\alpha\)-thujone (m. p. of the tribromide 121 to 122°; m. p. of the semicarbazone 186 to 188°). The oil also contained from 3 to 5\(^{\circ}/_{\circ}\) \(d\alpha\)-pinene, which was identified by its constants as well as by the preparation of its nitrosochloride. The authors further found the product to contain from 1 to 3\(^{\circ}/_{\circ}\) tanacetyl alcohol, which body was identified by its constants (b. p. 210 to 220; \(d_{250}\) 0,9266; \([\alpha]_{D250} +29,8^\circ\); \(n_{D250}\) 1,46207), and which appears to occur in the oil in the form of an acetate. Fenchone was not detected.

As the authors only quote the paper of Brandel and Dewey\(^1\) on oil of \textit{Thuja plicata}, it would appear that they have overlooked the work of Blasdale\(^2\) and our own communication on the subject\(^3\).

The oil obtained by us (yield 1,32\(^{\circ}/_{\circ}\)) from the air-dried leaves and branches gave the following constants: \(d_{150}\) 0,9056, \(\alpha_D + 5^\circ 4^\prime\), \(n_{D200}\) 1,45721, acid v. 0,8, ester v. 16,9.

\textbf{Thyme Oil} has remained very quiet. There have been plentiful arrivals of qualities rich in phenol, and the low prices have remained unchanged.

\textbf{Toddalia Oil.} The oil from the leaves of \textit{Toddalia asiatica}, L. (Kurz) \([T. aculeata,\) Pers.\(^4\) \] according to the \textit{Index Kewensis} has been distilled in the Philippines\(^5\) by Brooks. The yield was 0,08\(^{\circ}/_{\circ}\), and the constants were as follow: \(d_{500}^{25}\) 0,9059, \(n_{D500}\) 1,4620. During cooling there was precipitated 18\(^{\circ}/_{\circ}\) of a substance with an odour reminding of camphor, and very liable to decomposition, which, when recrystallised from light petroleum, melted between 96,5 and 97°. A fraction of the oil which boiled over between 195 and 200° contained linalool, which was identified by oxidation into citral.

\textbf{Trawas Leaf Oil.} The leaves of \textit{Litsea odorifera}, Valeton (N. O. Lauraceae), a native of Java, are known in that island as \textit{trawas} leaves and are in use as a popular remedy. According to van Romburgh\(^6\), they yield an essential oil possessing the following constants: \(d_{150}\) 0,836 to 0,846, \(\alpha_D - 0^\circ 10^\prime\) to \(-7^\circ\) (in a 200 mm. tube). The principal fraction of the oil boiled at 233° (120 to 125° at 10 mm.). With semicarbazide it formed a semicarbazone, m. p. 116°, from which a ketone was regenerated. This was treated by van Romburgh with permanganate of potassium, from which resulted a ketone, m. p. 12° (b. p. 234°; \(d_{170}\) 0,829; m. p. of the semicarbazone 124°), which proved to be methylbenzylketone. From the oxidation-liquid an acid \(C_{10}H_{18}O_3\), m. p. 49°, was isolated. This was 2-ketodecyclic acid, and, when oxidised with chromic acid and sulphuric acid, yielded suberic acid, while oxydation with sodium hypobromite.

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\(^{1}\) Pharm. Review 26 (1908), 248; comp. Report November 1908, 117.


\(^{3}\) Report April 1909, 89.

\(^{4}\) Comp. Gildeemeister and Hoffmann, \textit{The Volatile Oils}, p. 460.

\(^{5}\) Philippine Journ. of Sc. 4, A. (1911), 344.

resulted in azelaic acid and carbon tetrabromide. The unsaturated ketone which is present in the oil must therefore be nonylene-1-methylketone. As it was found impossible, by recrystallisation, to split up the semicarbazone from the original oil into its constituents, the ketone mixture which was regenerated from it was brominated, with a methyl alcoholic bromine solution, when hardly any portion of it reacted except the unsaturated ketone 1). After the saturated ketone had been distilled off the dibromide passed over at 204° (15 mm.). Upon the bromine being abstracted from the dibromide with zinc-dust and alcohol, there resulted a ketone, m. p. — 7°; b. p. 235°; d11.5° 0,848; mol. refr. 52,47, calc. for C10H20O1/2 52,51 2).

The alcohols of the trawas oil were separated by a similar method, and proved to be 1-methyl-\( n \)-nonylcarbinol (\( \alpha_D = 5^\circ 40' \)) and undecene-1-ol-10 (b. p. 233°; d100 0,835). Methyl\( n \)-nonylcarbinol was identified by oxidation into methyl-\( n \)-nonylketone; undecenol, when oxidised with chromic acid and sulphuric acid, yielded a ketone of which the semicarbazone had m. p. 113°; when oxidised with permanganate of potassium it yielded 2-ketodecylic acid.

An oil of which a sample was sent to us from Java many years ago under the name of "trawas olie" may here be mentioned. Its behaviour was as follows: d15° 0,9127, \( \alpha_D = 20^\circ 12' \), \( n\_D 0,14,6377 \), soluble in 1,1 vols a.m. 80°/° alcohol; the diluted solution showed slight opalescence. The oil was rich in cineole, as was evident from its odour, which also reminded of cardamoms.

**Turpentine Oil.** The method of turpentine-production by the new "cup and gutter" system, which we have repeatedly described in detail, has, according to an American Journal 3), the disadvantage that the cups employed for collecting the balsam are often upset by hogs and other animals which scour the forest for food. Many of the earthenware cups, no matter how carefully they are handled, are lost by breakage, and, finally, a good deal of the turpentine oil is wasted by evaporation. All drawbacks, as well as the danger of fire, are said to be obviated by a new method in which the collecting-vessel and the tapping-place in the tree are connected in an air-tight manner. This is done by boring into the sapwood of the tree a hole of 2 3/8 inches diameter, and not too deep. From the centre of this hole two other holes, 3/4 inch in diameter each, are bored steep upwards in a slanting direction, to the depth of a few

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1) According to Lobry de Bruyn [Berl. Berichte 26 (1893), 272] bromine acts much more slowly upon methyl alcohol than upon ethyl alcohol; hence the former is to be preferred for brominating purposes.

2) In this connection it should be borne in mind that possibly the ketone may still contain traces of saturated ketone which may be formed from the unsaturated ketone in the course of the treatment with zinc-dust.

3) Scientific American 105 (1911), 383.
inches. The rough bark surrounding the central opening is smoothed down to admit of the opening being closed with a flat cover. This cover communicates by means of a hollow prop with a second cover placed at right angles to the first, and into this second cover a glass receptacle, holding about one pint, is screwed air-tight. The turpentine collects first in the \( \frac{3}{4} \) inch holes, and flows thence through the wider hole and the hollow prop into the glass receptacle which, when full, is replaced by another. It is said that this new method possesses several advantages over those now in use. Among these, in addition to the avoidance of the disadvantages enumerated above, are the preservation of the trees, coupled with the possibility of tapping them for an unlimited period; the prevention of loss by running or evaporation and the avoidance of the costly and destructive process of preparing the drawing-surface by cutting.

It appears to us, at any rate at first sight, that the considerably higher cost-price of the glass receptacles and metal-parts as compared with the simple earthenware cups and tin-strips of the "cup and gutter" method, will be a disadvantage of the new process.

Numerous investigations, especially by French chemists, have shown the pinene of the Aleppo fir (Pinus halepensis) to be specially rich in pure \( d-a \)-pinene. On the other hand, Fernandez\(^1\) has found that the pinene from the Andalusian fir, which is identical with the Aleppo fir, is not quite identical with ordinary pinene. Unfortunately the abstract of Fernandez' paper before us gives no particulars of the constants of the pinene mentioned by him. He assumes the two pinenes to differ from each other because no nitrosites were obtainable from the Spanish pinene. When attacked by nitrogen tetroxide in the presence of acetic acid at \( 0^\circ \), a brownish-black body (probably an oxime) with a cymene-like odour was separated out. This body constituted about 55\% by weight of the pinene used. The corresponding pinene nitrolpiperidine constituted a spongy, non-crystalline mass. With toluidine, Fernandez obtained high-boiling fluids which distilled over between 130 and 141\(^\circ\) at 14 mm.; from the naphthylamines and the sulphanilic acid he was unable to obtain nitrolamines. The Spanish pinene only afforded 10\% crystalline terpene.

In the abstract at our disposal several points are left obscure. It is to be regretted that Fernandez does not state the constants of Spanish fir oil. We are uncertain what Fernandez means by his crystallised terpene, — whether camphene, prepared from conversion from the pinene hydrochloride or direct from the oil, or whether terpene? The fact that with aromatic bases such as aniline (and certainly also with homologous bases) pinene nitrosochloride does not afford nitrolamines, but pinene and amidoazobenzene is, we should think, generally known.

\(^1\) Chem. Ztg. 35 (1911), 1152. From a lecture.
To our several notes on Greek turpentine oil from *Pinus halepensis* we are now able to add the result of an examination by Parry who has found two authentic samples to possess the following characters:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{15o}$</td>
<td>0.8605</td>
<td>0.862</td>
</tr>
<tr>
<td>$\alpha_D$</td>
<td>$+36^\circ45'$</td>
<td>$+39^\circ$</td>
</tr>
<tr>
<td>$n_D_{20}$</td>
<td>1.4690</td>
<td>1.4736</td>
</tr>
<tr>
<td>Commences to distil at</td>
<td>$156^\circ$</td>
<td>$156^\circ$</td>
</tr>
<tr>
<td>Fraction 156 to $160^\circ$</td>
<td>$70%$</td>
<td>$72%$</td>
</tr>
<tr>
<td>$\alpha_D$ of 156 to $160^\circ$ fraction</td>
<td>$+37^\circ15'$</td>
<td>$+40^\circ$</td>
</tr>
</tbody>
</table>

In addition to the hydrocarbons l-pinene and sylvestrene, the presence of which in turpentine oil from *Pinus longifolia* we detected some time ago, H. H. Robinson, has found the oil to contain dipentene. Robinson is of opinion that possibly sylvestrene may not be present as such in the original oil, but that the oil may contain a hydrocarbon which, when treated with hydrochloric acid, yields a sylvestrene derivative, in the same way as a hydrochloride results from the treatment of pinene which by splitting off the latter yields camphene.

When the turpentine from the Douglas fir (*Pseudotsuga Douglasii*, Carr.) is distilled with steam under low pressure until all the turpentine oil has distilled over, there is left behind a clear, viscous yellow oil (Fir oil) which resembles the so-called pine oil from common turpentine. According to Walker, and also Teeple, this fir oil contains large proportions of terpineol. Benson and Darrin have examined a sample of fir oil, and found it to possess the following constants: m. p. below $–40^\circ$, $[\alpha]_{D20} = 37,6^\circ$, $n_D_{20} = 1,4818$; solubility in $70\%$ alcohol 49:100, acid v. 1,55, sap. v. 11,1, iodine value 185. From its constitution and its behaviour under fractionation, as well as from the readiness with which terpine hydrate was formed when the sample was treated with $5\%$ sulphuric acid, the authors conclude that at least one-third of the oil consists of terpineol, and that for many purposes it may be found to supply a substitute for pine oil.

Queysanne has proposed a purity-test for turpentine oil based upon its miscibility with aniline, and this same principle was subsequently adopted

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1) Report April 1905, 79; October 1905, 67; October 1909, 69.
2) Perfum. and Essent. Oil Record 2 (1911), 210.
3) Report April 1911, 116; October 1911, 93.
4) Proceed. chem. Soc. 27 (1911), 247.
5) Comp. Report November 1908, 125.
by Louise\textsuperscript{4}) in testing turpentine oil. The experiments of Queysanne with l\ae{}vorotatory French oil have been amplified by investigations conducted by Gallon\textsuperscript{5}). The samples of oil under examination possessed the following constants: \(d_{15} \text{0} 0,8675\) and \(0,8682\), \(n_{D_{20}} 1,4668\) and 1,4655, \(\alpha_{D_{19}} + 40,32^\circ\) and \(39,99^\circ\) respectively. The constants quoted in the second set of figures refer to another, but rather “older”, sample of the same oil, the difference in age being shown in the somewhat slighter solubility of the “older” sample. But on the whole, the dextrorotatory oil was not so soluble in aniline as the l\ae{}vorotatory sample which had previously been examined.

That the chemical testing of turpentine oil offers great difficulties is evident from the numerous publications on the subject. P. van der Wielen\textsuperscript{3}), who has been engaged in the investigation of this oil, proposes a modification of the sulphuric acid method. To 80 cc. sulphuric acid (d 1,698) in a flask of about 1 litre capacity, he adds 20 cc. of the oil under examination, and allows the mixture to stand for an hour under repeated shaking. After adding 300 cc. water the oil which has not been attacked is distilled over into a bottle with a graduated neck. The coefficient of refraction as well as the separation temperature of the solution in aniline are determined. It is also necessary to know the refraction of the original oil. According to van der Wielen, an addition of hydrocarbons\textsuperscript{4}) may be detected positively from the above data as well as from the quantity of oil which has not been polymerised by sulphuric acid. The author has examined by this method a large number of samples of turpentine oil as well as various substitutes and mixtures with benzene, hydrocarbons and carbon tetrachloride, and has collected the results in table-form.

For determining the evaporation-residue of turpentine oil, Herzfeld, and also Kollo\textsuperscript{5}) recommend the embedding of the platinum dish in a sand-bath, and the heating of the latter to \(155^\circ\) before filling-in the oil. In order to obviate the risk of explosion of the suddenly-generated vapour, a tin-ring is to be affixed below the rim of the dish. Wolff\textsuperscript{6}) has observed that when the dish is merely embedded in sand, the last particles of oil frequently creep over, and he obviates this trouble by surrounding the dish with a tin-cylinder about 2 inches in height and of a diameter exceeding that of the upper portion of the dish by nearly half an inch. This cylinder is stuck in the sand to a depth of about \(\frac{1}{4}\) inch.

\textsuperscript{2}) Comp. Report October 1910, 139.
\textsuperscript{3}) P. E. Gallon, \textit{Sur la solubilité réciproque de l'essence de térèbenthine dextrogyre et de vaniline}. Bordeaux 1911. From a reprint kindly sent to us.
\textsuperscript{4}) Pharm. Weekblad 8 (1911), No. 35.
\textsuperscript{5}) By hydrocarbons the author apparently understands petroleum-hydrocarbons.
\textsuperscript{6}) Comp. Report April 1910, 116.
\textsuperscript{7}) Farbenzeitung 16 (1911), 2746. Quoted from Chem. Zentralbl. 1911, II, 1181.
In view of the increasing importance of the so-called wood turpentine, as a result of the scarcity of genuine turpentine oil, the U. S. Department of Agriculture has caused two of its chemists, Messrs. Veitch and Donk, to report, in the detailed manner customary with this Department, upon the present experience relating to the production, refining and uses of wood turpentine. The report deals in the first place with the production of the oil by the various processes in use: destructive distillation, steam-distillation, and extraction with volatile and non-volatile solvents. Of these, steam-distillation produces the most useful oil. The distillate obtained by the destructive process, that is to say the fraction which distils over up to 170° and which is also called "wood turpentine" is quantitatively too small in comparison with the oils of higher b. p. Moreover, it is much more difficult to remove the characteristic pine-tar odour of this product by refining, than is the case with the oil obtained by steam-distillation. The method of extracting with volatile solvents is still in its infancy, but several plants use the method of extracting with hot rosin at 200°, which extracts the oil from the chipped wood. The rosin yields the oil to a current of superheated steam which is passed through it, and is afterwards used again for extracting fresh batches of wood. There is also a method of extracting the oil and resin from the wood by boiling the latter with soda liquor and removing the oil from the liquor with a steam-current before the rosin acids are precipitated; the cellulose of the raw material being worked up for paper. Of course the residual wood from the steam-distillation or the extraction with volatile solvents can also be made into paper-pulp or used for dry distillation.

Great importance is to be attached to the next process of purifying and fractionating the crude distillate, for which purpose a column-still either working intermittently or continuously, should be used. The distillate resulting from the destructive process is first freed from phenols by means of alkali and then refined by steam-distillation. Generally speaking, insufficient care is bestowed upon this work, and apparently the distillate is not fractionated; hence "carbonisation wood turpentine" is not to be regarded as a first-class product, owing to the considerable proportion of high-boiling oils contained in it. The portions of this oil which distil over between 80 and 154° closely resemble rosin spirits; the fraction boiling between 154 and 180° constitutes the destructively-distilled wood turpentine. It contains pinene, dipentene and other compounds which also occur in part in rosin spirits. The higher-boiling oils, with b. p. exceeding 180°, are mixtures of pine-tar and rosin oils in indefinite proportions and are used as greases and solvents, in the manufacture of printers' inks, &c. The constitution of the crude product of the steam-distillation of light wood

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is very different from the above. As a rule it is collected in the following two or three fractions: wood turpentine proper, b. p. 150—160° up to 175—180°; light pine-tar oil, b. p. 170—180° up to 210—225°; heavy pine-tar oil, b. p. 180—190° up to 230—240°. The first fractions contain chiefly pinene, also camphene, limonene, dipentene, and cineole, and (in case of careless fractionation) more or less terpinene, borneol, and terpineol. The pine-tar oil portions contain, in addition to small proportions of the terpenes, chiefly terpineol, borneol and fenchyl alcohol. A great many attempts have been made to free wood turpentine from its characteristic objectionable odour. It is true that the very first fractions of the steam-distilled oil have a pure odour, but the yield is too small to justify the rejection of subsequent fractions to make it practicable to collect them by themselves, and perhaps to disregard the succeeding fractions. Special experiments carried out by the Department have shown that the unpleasant odour attaches principally, although not entirely, to the higher boiling portions which are still included in the low-boiling fraction, and special importance is to be attached to the removal of these by carefully-conducted fractionation. When this is done, however, wood turpentine very closely resembles genuine turpentine oil, both in its odour and in its constitution. The following table shows the properties of the usual commercial turpentine oils:

<table>
<thead>
<tr>
<th>Constants</th>
<th>Gum Turpentine oil</th>
<th>Wood turpentine oil by destructive process</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_20^0)</td>
<td>0,8617 to 0,8889</td>
<td>0,859 to 0,915</td>
</tr>
<tr>
<td>(a_{20^0})</td>
<td>(-34,8^0 \pm 29,6^0)</td>
<td>(+16,5^0 \pm 36,14^0)</td>
</tr>
<tr>
<td>(n_{20^0})</td>
<td>1,4684 to 1,4818</td>
<td>1,4673 to 1,4755</td>
</tr>
<tr>
<td>Initial distilling point (uncorr.)</td>
<td>154°</td>
<td>153°</td>
</tr>
<tr>
<td>Distilling below 170°</td>
<td>73%</td>
<td>95%</td>
</tr>
<tr>
<td>Distilling below 185°</td>
<td>88%</td>
<td>98%</td>
</tr>
<tr>
<td>Iodine value according to Wijs</td>
<td>350 = 400</td>
<td>300 = 362</td>
</tr>
<tr>
<td>Acid v.</td>
<td>0,140 = 0,286</td>
<td>0,080 = 0,312</td>
</tr>
<tr>
<td>Sap. v.</td>
<td>2,44 = 8,60</td>
<td>1,06 = 8,75</td>
</tr>
<tr>
<td>Color (Lovibond)</td>
<td>for yellow</td>
<td>0,7 = 2,5</td>
</tr>
<tr>
<td></td>
<td>for red</td>
<td>0,0 = 0,5</td>
</tr>
</tbody>
</table>

The iodine-value is regarded as of significance, inasmuch as it indicates the proportion of heavy oil; but similar conclusions may be drawn from the saponification-value. Comparison of the crude with the rectified oils and their constants shows that rectification, as it is carried out in practice up to the present, hardly improves the quality, but only produces a distillate of a paler colour. The authors of the report go into full details on the subject of the experiments in fractionation which they conducted on a large scale, both in a simple and in a column still with direct steam. So far the record of the working showed no considerable difference
in the action of the two stills, but it is said that no definite judgment can yet be formed. So far as the evaluation of an oil-fraction in respect of its value as good, low-boiling wood turpentine is concerned, neither the often varying temperature of the steam which passes over, nor the specific gravity of the oil-particles is conclusive, but rather, according to practical experience, the respective proportions of oil and water in each fraction that distils over. The higher the proportion of oil, the more closely the properties of the oil approximate those of a good wood turpentine. When the total-distillate contains 55% oil or more, the proportion of good oil boiling below 170° is 90%; when the total proportion of oil ranges from 55 to 30%, renewed steam-distillation is needed in order again to obtain a light portion containing 55% of good oil (as before). Finally when the oil-content of the total distillate falls below 30%, it consists entirely of high-boiling oils, which it is unnecessary to try to work up for oils with b. p. below 170°.

With a view of deciding the important question to what extent the various wood turpentines could be used in the manufacture of paints and varnishes side by side with gum spirits, several varnishes were prepared with four samples of commercial oils, consisting of one sample each of guaranteed pure oil from gum of a steam-distilled wood turpentine, and two wood turpentines prepared by the destructive process and subsequently washed with soda and steam-distilled. In connection with these experiments it is expressly stated that, apart from one of the two samples last-mentioned, the wood oils contained large proportions of heavy oil, from which they derived a pronounced odour, and which caused the varnishes prepared with them to dry more slowly than usual. It is evident that varnishes prepared with oils of this description must give less satisfactory results than when a well-rectified oil had been used. From each of the four samples two kinds of varnishes were prepared, a coach finishing varnish and a piano varnish, with a view of testing their qualities under different atmospheric influences. We are unable to quote here the very detailed reproduction of the reports of the numerous firms which instituted these tests; partly preparing the varnishes themselves, and partly using them only. The disagreeable odour and the irritant action of the wood turpentine are generally commented upon; on the usefulness of the varnishes themselves the opinions differ. On the other hand the producers of wood turpentine of course claim that their productions are entirely suitable for the manufacture of paints, varnishes, &c.

We are now able to complete, on the authority of an American report, the particulars given in our last Report (p. 92) concerning the output of the various products of the American wood-distilling plants 1). From this

1) Oil, Paint and Drug Reporter 80 (1911), No. 26, p. 9.
it appears that in the year 1910 30 plants were engaged in the distillation of soft woods, principally yellow pine, together with small quantities of Norway pine and Douglas fir. The plants turned out an aggregate of 192,442 cords soft wood, as compared with 115,310, 99,212, and 62,349 cords in the years 1909 to 1907 — a proof of the increasing importance of the wood-turpentine industry.

In view of the large imports of Finnish and Swedish pine-tar oil into France, which are probably due principally to the prohibitive customs duty upon pure turpentine oil, a brief essay by Blarez and Vèzes\(^1\) on the properties of pine-tar oil from Northern Europe should be very useful to all those in France who are interested in oil of turpentine. In making comparisons between genuine turpentine oil and pine-tar oil, the following general characteristics of the latter chiefly deserve consideration: its very marked empyreumatic, unpleasant odour; its lower sp. gr. \((d_{950} 0.8520\) to \(0.8570\)); its lesser degree of volatility, a property which varies considerably in different samples; its higher co-efficient of refraction \((n_D 1.4700\) to \(1.4800\)) which also varies in the separate fractions, and, finally, its dextrorotation \((\alpha_D + 4\) to \(+5^\circ\)). Other points of difference are the readiness with which pine-tar oils dissolve in aniline, and Herzfeld's reaction. Mixtures of pine-tar oil with turpentine oil from the Landes may be detected and quantitatively estimated most readily by determining the rotation and by the temperature at which a mixture with known quantities of aniline separates.

To detect the presence of pine-tar oil in turpentine oil, Herzfeld has recommended the shaking of the latter with an equal volume of solution of sulphurous acid (yellow coloration denotes the presence of pine-tar oil; comp. Report April 1905, 78). Herzfeld has also recommended another test, consisting in pouring the oil under examination over a piece of caustic potash, when the presence of pine-tar oil is revealed by the caustic potash rapidly assuming a brown colour (Report April 1910, 110). H. Wolff\(^2\) has modified the last-named test by shaking up 0.5 to 1 cc. potash liquor \((d 1.3)\) with the oil, warming the mixture on the water-bath for 2 to 5 minutes, and then adding 3 cc. water to separate the emulsion. Pine-tar oil causes the aqueous layer to assume a brown colour, turpentine gives none, or only a very faint colour. Wolff gives two more tests for pine-tar oil which we quote below, without expressing an opinion on their value:

1. 5 cc. oil are brought to boiling with 5 drops nitrobenzene, when 2 cc. 25% hydrochloric acid are added and the mixture is kept

\(^1\) Sur l'essence de pin des pays du Nord de l'Europe. Bordeaux 1911. From a reprint kindly sent to us.

\(^2\) Farben Ztg. 17 (1911), 21, 78. Quoted from Chem. Ztg. Repert. 36 (1912), 64.
boiling for 10 seconds more. Pine-tar oil turns brown, the hydrochloric acid brown to black. Turpentine oil gives much paler tints.

2. To a mixture of 4 cc. each of ferric chloride \((1:2500)\) and potassium ferricyanide solution \((1:500)\) add from 2 to at most 10 drops of the oil to be tested and shake the whole vigorously. Pine-tar oil will rapidly give a copious precipitate of Prussian blue, whereas turpentine oil only gives a perceptible separation of that body after the lapse of some hours.

C. Piest\(^1\) proposes the following reaction to effect the same object: —

Shake in a test-tube 5 cc. acetic anhydride with 5 cc. turpentine oil, and add 10 drops concentrated hydrochloric acid while shaking and cooling. When the mixture has cooled down completely add, with shaking, 5 drops more of concentrated hydrochloric acid; this will cause the liquid to become warm and to make a clear solution. Turpentine oil then remains water-white, pine-tar oil turns black.

In every case the turpentine oil, whatever its origin, should be distilled before being tested.

In commenting upon a paper by Grimaldi on the detection of camphene in light resin oil and in other oils\(^2\), we took exception, in a footnote, to the use by Grimaldi of the designation “turpentine-essence” for light resin oil, because, especially in translating, the term encourages confusion with turpentine oil. In a letter which he has addressed to us Grimaldi disowns the authorship of the term, and declares that he has taken it from a paper by Valenta\(^3\), who may possibly have borrowed it himself. It is also necessary, Grimaldi observes, to differentiate between turpentine essence, and light resin oils or pinoline; the last-named being that product of the distillation of colophony which passes over at up to about 230°, whereas “turpentine essence” constitutes the most volatile fractions of that distillation, boiling over between 160 and 170°.

We admit that in our footnote we drew no such sharp distinction between the two distillates, as we did in previous Reports\(^4\). That, anyhow, was not our principal object, which was chiefly to enter a protest against the use of the name “turpentine essence” as inappropriate, without, however, expressing an opinion on the authorship of the term. And on the point to which we attach the most importance, Grimaldi agrees with us.

**Valerian Oil.** We always have at our disposal considerable quantities of superior oil of our own distilling and shall be pleased to submit special offers when quantities of some importance are in question. This article

\(^1\) Chem. Ztg. 36 (1912), 198.
\(^2\) Report April 1911, 118.
\(^3\) Chem. Ztg. 29 (1905), 807; Report October 1905, 70.
\(^4\) As, for example, Report October 1905, 71; April 1908, 105.
has acquired a wide circle of regular customers within the past decade or two, especially among tobacco manufacturers.

**Vetiver Oil.** We have always at our disposal a considerable stock of excellent oil of our own distilling, and we are therefore in a position to pick out from the arrivals of vetiver root (which are notoriously irregular) those parcels which are richest in perfume and most suitable for our purposes. The quality of our distillate is unapproached, and in the preparation of really fine perfumes its employment is indispensable. Réunion vetiver oil continues to be firm. It is true that the exports in the year 1911 reached 975 kilos, and are therefore but little below those of the previous year, when they amounted to 1007 kilos, but reports dated December 31st state that there are no further supplies in the island. If the production should really be restricted, at it is said will be the case, the prices would of course be correspondingly affected. But so many contradictory statements have obtained currency concerning those articles of produce from Réunion which are of interest to us, that as a matter of course we regard the above report with the same scepticism as the rest.

The experiments in cultivation which have been carried out at Buitenzorg with the *Akar wangi* plant, the non-flowering variety of *Andropogon muricatus* which occurs in Java), have shown that when grown in the shade the production of root is unfavourably affected, whereas repeated cutting of the plant has a favourable effect upon the development of the roots.

**Walnut Leaf Oil.** As, generally speaking, very little is known of the properties of walnut leaf oil, the following note on two oils, one of which was distilled by us at Miltitz and the other at Barrême, may be of interest. The distillates were of an olive-brown colour and possessed the characteristic odour of walnut-leaves. At about 10° they formed semi-solid, butter-like masses, which melted at about 20°. From the solutions in 90% alcohol large quantities of paraffin separated out, which after repeated recrystallisation from alcohol gave m. p. 61 to 62°. The constants of the oil are shown in the table below, and in connection with

<table>
<thead>
<tr>
<th>Distilled at</th>
<th>Yield</th>
<th>d₂₀₀</th>
<th>α₀</th>
<th>n₀₂₅₀</th>
<th>Acid v.</th>
<th>Ester v.</th>
<th>Ester v. after acet.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miltitz</td>
<td>0,014%</td>
<td>0,9137</td>
<td>±0°</td>
<td>1,49657</td>
<td>9,3</td>
<td>27,0</td>
<td>-</td>
</tr>
<tr>
<td>Barrême</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>83% Principal oil</td>
<td>0,0072%</td>
<td>0,9174</td>
<td>-17° 36’</td>
<td>1,49177</td>
<td>3,7</td>
<td>9,3</td>
<td>-</td>
</tr>
<tr>
<td>17% Water oil</td>
<td>0,0015%</td>
<td>0,9231</td>
<td>-16° 12’</td>
<td>1,49366</td>
<td>4,7</td>
<td>9,7</td>
<td>-</td>
</tr>
<tr>
<td>100% Total oil</td>
<td>0,0087%</td>
<td>0,9185</td>
<td>-17° 0’</td>
<td>1,49215</td>
<td>—</td>
<td>—</td>
<td>98,5</td>
</tr>
</tbody>
</table>

1) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 48.
these figures it should be stated that we examined, of the Barrême oil, first the distillate which had separated out directly in the receiver, next the oil obtained by extracting the distillation-water with ether, and lastly the total oil as represented by pouring together the two fractions.

It will be noticed that there are certain differences between the Miltitz and the Barrême oils, chiefly expressed in the optical behaviour.

**Oil of Watermint.** According to K. Irk, Hungarian oil of *Mentha aquatica* possesses the following constants: \( d_{15}^{20} 0.9603, \ a_{D}^{20} + 22.73^{\circ}, \ n_{D}^{20} 1.4900, \) sol. in 0.5 vols. of 90\%/ alcohol. The oil is of a dark straw colour and possesses an agreeable odour reminding of pennyroyal. In its constants the oil shows a marked difference from an oil from Spanish herb described by Schimmel & Co.\(^{3}\).

**Wintergreen Oil, Indian.** From 3.3 kilos of the leaves and stalks of *Gaultheria punctata*, Bl. (*G. fragrantissima*, Wall., comp. our last Report, p. 96) there was obtained at Buitenzorg\(^{2}\) 23 cc. of oil with a density of \( d_{20} 1.175, \ a_{D} + 0^{\circ} \); sap. v. 234 (after 1 hour), 289 (after 2 hours), 357 (after 3 hours), 360.6 (after 4 hours), corresponding to 97.9\%/ methyl salicylate.

The leaves and stalks of *Gaultheria leucocarpa*, Bl. (880 grams) have also been distilled, yielding 3 cc. oil. Sap. v. after 2 hours 332.

**Wormseed Oil, American.** American wormseed oil still remains scarce and dear and appears inclined at the very least to maintain its present level of value.

Our New York branch reports that it is extremely difficult to procure trustworthy data concerning the crop from the growing districts in Maryland, but the result is estimated not to exceed one-half of the average of previous years.

**Wormwood Oil.** Our New York friends report that the result of the American crop has fallen far below the original estimate and that, owing to the unfavourable climatic conditions, the contracts for delivery which had been concluded before the beginning of the distilling season have only been carried out to the extent of about 50 per cent. The prices have remained at their previous level, and would certainly have advanced considerably if the demand had not given way to an appreciable extent. This last statement is confirmed by our own experience of the American wormwood oil trade. This stagnation in the demand is doubtless in part attributable to the fact that in the European market the German wormwood oil distilled by ourselves is so popular that it would be preferred.

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1) Kiserletügyi Közlemények 14 (1911). From a reprint kindly sent to us. Also see Pharm. Zentralh. 52 (1911), 1111.
3) Jaarb. dep. lantb. in Ned.-Indië, Batavia 1910, 47.
to American oil owing to its lower price alone, if for no other reasons. In respect of quality our German oil fulfills the most exacting requirements, and the employment of a more expensive quality is therefore merely a luxury. Our plantations have stood the winter well and will no doubt this year again produce sufficient oil for our requirements.

We hear that there is some intention of prohibiting entirely the consumption of absinth in France, and that a Bill to this effect is to be introduced before long in the Chamber of Deputies.

**Xanthoxylum Oils.** E. M. Holmes¹ states that under the name of "Japanese pepper" a fruit has recently made its appearance upon the English market which is distinctly different from the fruit of *Xanthoxylum piperitum*, D. C., (usually known as Japanese pepper) and which no doubt really belongs to the species *X. alatum*, Roxb.⁵. According to an article by Umney which constitutes an amplification of the note by Holmes, the oil distilled from the above-named fruit was pale yellow in colour and had an odour resembling a mixture of lime and nutmeg; d 0,889, α₀ — 23⁰. After standing for a few days crystals of stearoptene separated in the form of long, white needles, m. p. 80⁰; for the rest the oil was found to consist chiefly of terpenes, boiling between 170 and 200⁰. Umney believes the oil to be identical with one previously examined by J. Stenhouse⁶. It is true that the latter stated that his oil was obtained from the fruit of *Xanthoxylum piperitum*, but according to Holmes, Stenhouse erroneously referred to the fruit from which his oil was prepared as *Xanthoxylum piperitum*. In reality it was that of *X. alatum*, a circumstance to which Hanbury had already previously drawn attention.

We may add to the above that in our Report of October 1910, 147, we gave detailed particulars of an oil distilled by us from the fruit of *Xanthoxylum alatum*, Roxb., a fact which has been completely overlooked both by Holmes and by Umney. In the present Report (see next page) we refer to a further examination of our oil by Semmler and Schossberger, from which it appears that the crystals which are separated from the oil (the "xanthoxyline" of Stenhouse) agree with phloracetophenone dimethyl-ether, while the terpenes ("xanthoxylene") are possibly identical with l-sabinene. It is probable that Holmes and Umney are correct in their assumption that the parent-plant of the oil examined by Stenhouse was *X. alatum* and *X. piperitum*, inasmuch as the constituents of the oil found by Stenhouse clearly point to *X. alatum*. Moreover, citral, which is a characteristic constituent of the oil of *X. piperitum*, and the presence of which is expressed in the odour of that oil, was absent, both from the oil obtained by us and from that distilled by Umney.

¹ Perfum. and Essent. Oil Record 3 (1912), 37.
² These fruits are known in Japan as "Fuyu Sansho", i. e. "Winter Sansho", the designation "Sansho" being applied exclusively to the fruit of *X. piperitum*.
³ Pharmaceutical Journ. 1 17 (1357), 19; Liebigs Annalen 104 (1857), 236.
The fruit of *X. piperitum* had been distilled by us many years previously and at that time (Report October 1890, 61) we also made a brief reference to the oil. A small sample of the fruit distilled at that time was still available and this we have again submitted to botanical examination, as a result of which we have confirmed its derivation from *X. piperitum*.

The oils obtained from *Xanthoxylum Aubertia*, D. C., and from *X. alatum*, Roxb., to which we have briefly referred in previous Reports¹, have been thoroughly investigated by Semmler and Schossberger². They found the first-named oil to contain an aliphatic terpene, related to ocimene and alloocimene, and possessing the following properties: \( d_{20} 0.8248, \alpha_D + 30^\circ, n_D 1.49775 \). The high-boiling fractions of the oil contained a hitherto unknown, monocyclic sesquiterpene, to which the authors gave the name of evodene (b. p. 119 to 123⁰ at 9 mm.; \( d_{20} 0.8781; \alpha_D - 58^\circ; n_D 1.49900 \)). Semmler and Schossberger also showed the oil to contain from 40 to 60% methyleugenol, which they identified from its oxidation-product, veratrlic acid (m. p. 180 to 181⁰). After being heated with amylalcoholic potash liquor the refraction of the methyleugenol-fraction was considerably higher than before, from which follows that the oil contains methyleugenol and not methylisoeugenol. The fractions with the highest b. p. contained phloracetophenone dimethylether³) a body of which the presence in oil of *Blumea balsamifera* was demonstrated in our laboratory some time ago⁴).

In the oil of *Xanthoxylum alatum* the authors discovered a terpene which they call xanthoxylene⁵), but which is perhaps identical with \( l \)-sabinene. This terpene yields a monohydrochloride, b. p. 83 to 87⁰ (10 mm.), \( d_{20} 0.959, \alpha_D - 11^\circ, n_D 1.4824 \); reduction of the latter with sodium and alcohol giving rise to a hydrocarbon \( C_{16}H_{18} \) with the following constants: b. p. 52 to 58⁰ (9 mm.), \( d_{20} 0.8275, \alpha_D - 17^\circ, n_D 1.4582 \). When ozonised, xanthoxylene forms a ketone of which the semicarbazone has b. p. 123⁰, whereas the m. p. of the sabinene ketone semicarbazone is 141⁰. Other constituents of the oil are phloracetophenone dimethylether and also perhaps cuminic aldehyde. The phloracetophenone dimethylether separates out from the oil at ordinary temperature in the form of a solid mass. This ether was characterised by its monobromide (m. p. 187⁰), its methyl derive (m. p. 103⁰), and its acetyl derive (m. p. 107⁰).

**Ylang-Ylang Oil.** Generally speaking the trade in ylang-ylang oil has been exceedingly flat, although the regular supplies of our "Sartorius"

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¹) Report April 1907, 105; October 1910, 147.
²) Berl. Berichte 44 (1911), 2885.
³) As regards characterisation see below.
⁵) The name "Xanthoxylene" has already been introduced by Stenhouse on a previous occasion, obviously for the same terpene. [Pharmaceutical Journ. I. 17 (1857), 19; Liebig's Annalen 104 (1857), 235; see also previous page.
brand, owing to their exquisite quality, have not been difficult to place, and our stocks in warehouse therefore never exceed a few original cases. It is true that the cheap Réunion oils, as has already been frequently pointed out by us, cannot approach the best reputed Manila brands in respect of quality, but it is nevertheless not surprising that French consumers in particular should evince a steadily-growing interest in this new product of the French Colonies. To this must be added the general tendency to buy low-priced goods, although as a matter of fact this tendency is wholly misplaced in the case of such fine products as ylang-ylang oil. The shipments of ylang-ylang oil from Réunion have declined from 2363 kilos in 1910 to 856 kilos in 1911, but in view of the enormous stocks which have been carried over from the year 1910, this decline has had no effect whatever upon the market-value.

In connection with an incident which has occurred in England we again take this opportunity to place upon record the fact that the sale of the "Sartorius" brand is entirely controlled by us, and that the brand is legally protected in all civilized countries.

An article by B. T. Brooks¹) deals with the fluctuations in the market-values of ylang-ylang oil. He ascribes the fall in the prices mainly to the ever-increasing over-production, a fact upon which we have also laid stress on several occasions. Ten years ago, when the prices rose as a result of the political disturbances in the Philippines, the planting of ylang-ylang trees was quickly taken up in many localities, especially in Java, Jamaica, Bangkok, Tonquin, Nossi-Bé, Mayotte, and the Comoro Islands. The oils distilled in all these localities, however, are only of secondary quality and cannot compete with the first-class Philippine oils. As we have regularly reported on the production of ylang-ylang in the several countries named, this short reference to Brooks's article will be sufficient, especially because he bases himself chiefly upon our statements and upon those of Roure-Bertrand Fils.

Three years ago²) we reported on an ylang-ylang oil which had been obtained by Bacon by the extraction method and of which the odour differed somewhat from that of the distilled oil. Bacon explained this difference by the presence of compounds very liable to decomposition which were destroyed in the process of steam-distillation. In order to discover to what extent ylang-ylang oil undergoes a change when heated with water, Brooks³) heated a mixture of 5 grams of the oil with 15 cc. water on an oil-bath to a temperature of from 105 to 120° for 5 hours. At the end of that time the saponification value of the oil showed a drop

¹) Philippine Journ. of Sc. 6, A. (1911), 355.
²) Report October 1909, 131.
³) Philippine Journ. of Sc. 6, A. (1911), 349.
of from 2 to 4 units. Brooks seeks to explain the differences in quality between ylang-ylang oils of the first and of the second class by a slight decomposition of the esters during the distilling of the flowers.

Two ylang-ylang oils which had been received by the firm of Roure-Bertrand Fils\(^1\) from Mayotte showed the following differences in constants: \(d_{150} 0,9594\) and \(0,9651, \alpha_d - 53°56'\) and \(-45°16'\), acid v. 1,3 and 1,4, ester v. 129,7 and 131,6, ester v. after acetylation 167 and 180,8, soluble in 1 vol. 95\% alcohol, cloudiness ensuing when more alcohol was added. A third sample gave the unusually low optical rotation of \(-4°4'\).

**Zedoary Seed Oil.** It has not yet been possible to procure supplies of this oil, but consumers appear to have reconciled themselves to the lack of the article, for the demand has entirely ceased.

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**New Essential Oils.**

**Oil of Aframomum angustifolium.** From the seed of a species of cardamoms indigenous in German East Africa, of which a sample had been sent to us from Usambara, we obtained by distillation 4,5\% of a colourless oil possessing the following characters: \(d_{150} 0,9017, \alpha_d - 16°50'\), \(n_{D200} 1,46911\), acid v. 0,4, ester v. 4,2, sol. in 6 vols. a. m. 80\% alcohol. So far as aroma is concerned it cannot compare with Ceylon cardamom oil, and owing to its high cineole-content it reminds rather of cajuput oil. Unfortunately the quantity of oil placed at our disposal was too small to enable us to estimate its constitution with any exactitude. Botanical examination of the entire fruit showed that the seed was derived from *Aframomum angustifolium, K. Schum.*\(^2\) (N. O. Zingiberaceæ), a plant which occurs also in Madagascar and in the Seychelles Islands.

The Cameroon-cardamoms\(^3\), which yield an oil similar in every respect to the above, and wich also closely resemble the Usambara-fruit in appearance, are (according to a special definition made by our authority, Dr. Giessler) derived from another species, *viz., Aframomum Daniellii, K. Schum.* (Amomum Danielli, Hook. f.). Sadebeck's\(^4\) assertion that

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1) Berichte von Roure-Bertrand Fils, October 1911, 43.
2) According to K. Schumann's monograph on the Zingiberaceæ (Engler's *Pflanzenreich*, Part 20), the following are synonymous: *Amomum angustifolium*, Sonnerat, *A. madagascariense*, Lam., *A. nemerosum*, Boj. and *A. sanctabaricum*, Worth. This nomenclature does not quite agree with the *Index Kewensis*, but the latter is no longer authoritative so far as concerns the matter here at issue.
the parent-plant of the Cameroon-cardamoms is *Amomum angustifolium*, Sonnerat, is incorrect, and the same applies to the statement in a notice on the cardamoms of tropical West Africa by D. Hanbury [Pharmaceutical Journal III. 2 (1872), 642] in which *Amomum Daniellii*, Hook. and *A. angustifolium*, Sonnerat are said to be identical.

**Pharmacopoeias.**

**The British Pharmaceutical Codex 1911.**

A new Edition has appeared of the British Pharmaceutical Codex, which was first published by the Pharmaceutical Society of Great Britain in the year 1907. As the Codex deals with a number of articles pertaining to our trade, we took occasion at the time to comment upon these articles in our Report¹). Unfortunately, our criticism has not had the result at which we aimed, for upon perusing the new Edition we observe that many erroneous statements have been transferred into it from the first Edition, although we also notice that numerous mistakes have been corrected. As the Codex is only a guide for pharmacists, and has no official force, we forbear, as regards the majority of articles to be quoted, from useless repetition, and will limit ourselves in the present review to the consideration of changes and amplifications, referring for the rest to our previous criticism. The above applies specially to any incorrect data which have been incorporated into the new from the old Edition, and which for that reason are not again criticized here. Similarly we refrain from mentioning articles in which no alterations have been made. None of the oils and preparations mentioned in the first Edition have been omitted from the second, while citronella oil has been newly added.

**Ajowan Oil** (*Oleum Ajowan*). \( d_{15.5^°} 0.917 \text{ to } 0.930 \)¹).

¹) The minimum limit is too high; in the first Ed. it was given correctly as 0.900.

**Anethol.** \( a_D \pm 0^° \).

**Anise Oil, Star Anise Oil** (*Oleum Anisi*). \( d_{20^°} 0.975 \text{ to } 0.990; \ a_D \) lævorotatory, up to \( -2^° \), occasionally slightly dextrorotatory; m. p. usually about 17°.

**Bay Oil** (*Oleum Pimentm Foliorum*). \( d_{15.5^°} 0.945 \text{ to } 0.975 \)¹); \( a_D \) slightly lævorotatory, up to \( -6^° \); phenol-content 40 to 65%.

¹) The maximum limit is too low, and should be raised to at least 0.985.

¹) Report April 1908, 134.
Bergamot Oil (Oleum Bergamotae). \( \alpha_D + 8 \text{ to } \pm 20^\circ \), occasionally higher; evaporation residue 5 to 6/o.\(^1\).

Bitter Almond Oil (Oleum Amygdalæ amarae). The oil containing hydrocyanic acid is now incorporated in lieu of the oil free from hydrocyanic acid. Colourless\(^1\); \( d_{15,50} 1,045 \text{ to } 1,060; \alpha_D \pm 0^\circ \); b. p. 179\(^0\); sol. in any proportion in 90/o alcohol. The natural oil may contain from 4 to 5/o hydrocyanic acid; oil to be used for medicinal purposes should contain from 2 to 4/o hydrocyanic acid. Test for the absence of chlorides and nitrobenzene.

\(^1\) The minimum limit should be reduced to 4,5.

Cajuput Oil (Oleum Cajuputi). \( d_{15,50} 0,919 \text{ to } 0,930; \alpha_D \) laevorotatory up to \(- 4^\circ\).

Camphor (Camphora). M. p. 175 to 179\(^0\).

Camphor Oil (Oleum Camphoræ essentiale). \( d_{15,50} \) after removal of the safrol about 0,960. Heavy camphor oil containing safrol has \( d_{15,50} 1,000 \) to 1,025; light camphor oil has \( d_{15,50} 0,890 \) to 0,920 and \( \alpha_D + 16 \text{ to } + 30^\circ\).\(^1\) As in the first Edition, it is again correctly stated that no definite standards can be given concerning its properties.

Caraway Oil (Oleum Carui). \( \alpha_D + 70 \text{ to } + 82^\circ \); carvone-content 45 to 60/o.

Cassia Oil (Oleum Cassiae). \( d_{15,50} 1,055 \text{ to } 1,070; \) lead test\(^1\).

Cedar Wood Oil (Oleum Cedri). \( d_{15,50} 0,940 \) to 0,950; \( \alpha_D - 30 \text{ to } - 45^\circ.\)

\(^1\) For the maximum limit 0,961 would be a more correct value.

Chamomile Oil, German (Oleum Matricariae Chamomillæ). \( d_{15,50} 0,930 \) to 0,940\(^1\).

\(^1\) The sp. gr. ranges from 0,924 to 0,945.

Cinnamon Oil, Ceylon (Oleum Cinnamomi). \( d_{15,50} 1,000 \text{ to } 1,030\).\(^1\)

Cinnamic aldehyde content about 55 to 65/o.\(^3\).

\(^1\) The sp. gr. of normal Ceylon cinnamon oil ranges from 1,023 to 1,040.

\(^3\) Normal oil contains from 65 to 75/o cinnamic aldehyde. Comp. Report October 1910, 35.

Citronella Oil (Oleum Citronellæ). Nearly colourless\(^1\) or pale yellow; \( d_{15,50} 0,900 \) to 0,920 (for Java oil not below 0,885); \( \alpha_D \) usually between 0 and \(- 15^\circ \); sol. in 3 to 10 parts 80/o alcohol without turbidity. Total geraniol in Java oil 80 to 90/o, in Ceylon oil 55 to 65/o.

\(^1\) Ceylon Citronella Oil is generally yellow to yellowish brown.

Clove Oil (Oleum Caryophylli). \( d_{15,50} 1,047 \text{ to } 1,065; \alpha_D \) laevorotatory, up to \(- 1^\circ 30' \); sol. in 3 vols. 70/o alcohol.

Copaiba Oil (Oleum Copaibæ). \( d_{15,50} 0,896 \) to 0,910.
Coriander Oil (*Oleum Coriandri*). \( a_D = +8 \text{ to } +14^\circ \), occasionally lower 1).

1) We have never observed pure oil with \( a_D \) lower than \( +8^\circ \).

Cubeb Oil (*Oleum Cubebe*). \( d_{15,5^\circ} = 0,910 \text{ to } 0,930; \quad a_D = 25 \text{ to } -40^\circ \).

Dill Oil (*Oleum Anethi*). \( d_{15,5^\circ} = 0,900 \text{ to } 0,915^1); \quad a_D = 70 \text{ to } +80^\circ, \) sol. in 3 vols. 90\%/ alcohol.

1) The minimum limit is too high; it should be 0,895.

Eucalyptus Oil (*Oleum Eucalypti*). \( d_{15,5^\circ} = 0,910 \text{ to } 0,930. \)

Fennel Oil (*Oleum Foeniculi*). \( d_{15,5^\circ} = 0,960 \text{ to } 0,990^1). \)

1) The maximum limit was given more correctly in the 1907 Edition as 0,980.

Juniper Oil (*Oleum Juniperi*). \( d_{15,5^\circ} = 0,862 \text{ to } 0,890^4); \quad a_D \text{ usually about } -4 \text{ to } -6^\circ, \) rarely exceeding \(-12^\circ\). Oil from the leaves and branches has opt. rot. about \(+8,5^\circ\).

1) We have found commercial oils of good quality to possess a sp. gr. of 0,860.

Lavender Oil (*Oleum Lavandulae*). \( d_{15,5^\circ} = 0,882 \text{ to } 0,900; \) ester content (linalyl acetate) 7 to 11\%/ (English oil) and 25 to 45\%/ (French oil) 1).

1) In the case of steam-distilled oils as much as over 50\% is observed.

Lemon Oil (*Oleum Limonis*). \( a_D = +58 \text{ to } +65^\circ, \) occasionally up to \(+66^\circ\); the optical test for the first 10\% of the distillate has been omitted. Terpene-free lemon oil 1): \( d_{15,5^\circ} = 0,895 \text{ to } 0,900; \quad a_D = 5 \text{ to } -8^\circ; \) citral content 40 to 50\%/.

1) It is impossible to lay down definite limits of value for terpene-free oils, as their properties vary according to the process of manufacture.

Lemongrass Oil 1) (*Oleum Graminis citrati*). \( d_{15,5^\circ} = 0,895 \text{ to } 0,905; \) in West Indian Oil 0,878 to 0,882 2); minimum citral content (bisulphite method) 70\%/.

1) *Andropogon citratus*, D. C. is mentioned as the parent-plant, a designation which, according to the most recent investigations, applies only to the variety of lemongrass which yields the imperfectly-soluble oil. Comp. Report April 1907, 33, 34.

2) In this case also the sp. gr. is very frequently considerably higher.

Mustard Oil (*Oleum Sinapis volatile*). B. p. 147 to 156\^.

Nutmeg Oil (*Oleum Myristicae*). \( d_{15,5^\circ} = 0,870 \text{ to } 0,930; \quad a_D = 13 \text{ to } +30^\circ 1); \) sol. in 3 vols. 90\%/ alcohol.

1) Oils prepared in our own works have given opt. rot. as low as \(+7^\circ 52^\prime\). Comp. Report October 1904, 66.

Orange Oil (*Oleum Aurantii*). \( d_{15,5^\circ} = 0,847 \text{ to } 0,854^1); \quad a_D = 95^\circ (\text{or } 92^\circ \text{ for bitter oil})^2 \text{ to } +98^\circ. \)

1) In Bitter Orange Oil the sp. gr. ranges from 0,852 to 0,857; in sweet oil from 0,848 to 0,853.

2) We have observed a minimum of 89\° in bitter oil of unquestionably reliable origin.

Pennyroyal Oil (*Oleum Pulegii*). \( a_D = 13 \text{ to } +35^\circ. \)

Peppermint Oil (*Oleum Mentha piperitae*). \( a_D = 18 \text{ to } -35^\circ, \) rectified oil is soluble in 4 vols. of alcohol (70\%/).
Pimento Oil (Oleum Pimenta).  $d_{15.5°} 1.030$ to $1.050^1$, eugenol content $60$ to $75\%/0^2$.

1) We have observed a minimum of $1.024$ in oils distilled by ourselves.

2) We have observed up to $80\%/0$ in our own distillates. The estimation must be carried out with $3\%/0$ solution, as otherwise the results are too high.

Pine Oil (Oleum Pinus).  $d_{15.5°} 0.865$ to $0.870^1$; $\alpha_D = 5$ to $-10^\circ$.

1) We have already pointed out on a previous occasion (Comp. Report October 1906, 62), that of recent years numerous oils of Pinus Pumilio are brought into commerce which show a lower sp. gr. and a higher opt. rot. and yet are of exquisite quality. In judging the properties of an oil this fact should be taken into account.

Pine Oil, Siberian (Oleum Pini Sibirica).  $d_{15.5°} 0.900$ to $0.920$; $\alpha_D - 30$ to $-42^\circ$; bornyl acetate content $30$ to $40\%/0$.

Geranium Oil (Oleum Geranii).  $d_{15.5°} 0.890$ to $0.906$. Bourbon oils $0.885$ to $0.895$; ester content (geranyl tiglate) of the French oils $23$ to $29\%/0$, of the Algerian oils $25$ to $28\%/0$ and of the Bourbon oils $30$ to $35\%/0^1$.

1) We have found Algerian oils to contain from $13$ up to $23.5\%/0$ and Bourbon oils from $21$ up to $33\%/0$ geranyl tiglate.

Rose Oil (Oleum Rosea).  $d_{15.5°} 0.854$ to $0.862^1$; $\alpha_D = 2$ to $-4^\circ$; $n_{D20°} 1.460$ to $1.465^3$; cong. pt. $+18$ to $+22^\circ$, usually about $20^\circ$.

1) The minimum limit given is too high; it should be $0.849$.

2) We have found oils of good quality with opt. rot. down to $-1^\circ$. Comp. also p. 108 of the present Report.

3) The co-efficient of refraction of good Bulgarian oils, according to our experience, is frequently lower; we have observed a minimum of $1.452$.

Rosemary Oil (Oleum Rosmarini).  $d_{15.5°} 0.895$ to $0.920$; $\alpha_D$ usually dextrorotatory, $+1$ to $+12^\circ$, English and Spanish oils are often slightly laevorotatory; sol. in $5$ to $10$ vols. $80\%/0$ alcohol. Borneol content $10$ to $16\%/0$, bornyl acetate content $2$ to $5\%/0$. The estimation of the rotation of the initial $10\%/0$ of the distillate is omitted.

Rue Oil (Oleum Ruta).  $\alpha_D + 0^\circ 13'$ to $+2^\circ 30'$.

1) We have already pointed out on the occasion of our previous criticism that faintly laevorotatory rue oils are occasionally met with.

Sandalwood Oil, East Indian (Oleum Santali).  $d_{15.5°} 0.973$ to $0.984$; $\alpha_D = 13$ to $21^\circ$. Santalol-content ($C_{10}H_{24}O$) not less than $90\%/0$, generally $92$ to $98\%/0$.

Savin Oil (Oleum Sabinae). The oil distilled from Juniperus phœnicea has a lower sp. gr. ($d_{15.5°}$ about $0.890$) and a lower optical rotation ($\alpha_D + 4$ to $+5^\circ$) than has true savin oil$^1$.

1) Comp. with regard to this Report April 1906, 61; October 1906, 72; April 1907, 93.

Spearmint Oil (Oleum Menthae viridis).  $\alpha_D = 36$ to $50^\circ$.

Thyme Oil (Oleum Thymi). Phenol-content $20$ to $45\%/0$, to be estimated with $5\%/0$ solution; usually $3$ parts of $70\%/0$ alcohol are required to dissolve the oil, though sometimes $10$ or more.
Turpentine Oil (Oleum Terebinthinae). $\alpha_D$ of the American variety almost invariably dextrorotatory, $+1$ to $+15^\circ$, occasionally also slightly laevorotatory.

Turpentine Oil, Rectified (Oleum Terebinthinae rectificatum). $d_{25}^5$ 0,860 to 0,865¹ (U. S. Ph.).

¹ The minimum limit of value relates to a temperature of $15^\circ$, for $d_{25}^5$ it is 0,853.

Wintergreen Oil, Natural.

a) Oleum Betulae (from Betula lenta, L.). $d_{15,5} 1,179$ to 1,187; sol. in 6 vols. $70\%$ alcohol.

b) Oleum Gautheriae (from Gaultheria procumbens, L.). $d_{15,5} 1,180$ to 1,187; sol. in 6 vols. $70\%$ alcohol.

Wormseed Oil, American (Oleum Chenopodi). $d_{15,5} 0,970$ to 0,990¹; $\alpha_D$ $-1$ to $-6^\circ$.

¹ The minimum limit is too low. Comp. Report April 1908, 109.

Japanese Pharmacopoeia.

The Deutsche Japanpost of January 20, 1912 (No. 43, p. 14), contains an article on additions to and alterations in the Pharm. Japonica III. Among the preparations there mentioned is sandalwood oil, which is thus referred to:

"Oleum Santali is a viscous, pale yellow or yellow, optically active liquid ($\alpha_{D20} = 16$ to $-20^\circ$). Its b. p. lies between 275 and 280°, at 292 to 300° it loses over $70\%$ in weight. When two drops of Oleum Santali are introduced into a mixture consisting of 9 cc. glacial acetic acid and 1 cc. hydrochloric acid, the solution should not acquire a red or violet colour within the lapse of 5 minutes."

It is not clear from the article in question whether these data are already officially in force, or whether they relate to proposed alterations only, as the "additions and alterations" are published without any comment. Apart from the optical rotation, however, the amplifications cannot be described as a happy selection. It would have been better if no details had been given of the boiling point, or rather of the boiling temperature, especially in view of the fact that those mentioned above are not even correct. If the distillation is carried out in the proper manner, that is to say so that the entire mercury-column of the thermometer is surrounded by the vapour arising from the liquid, it will be found that only a very small portion of the oil (about $10\%$) passes over below 300°, which is quite natural, seeing that the b. p. of santalol, which forms over $90\%$ of the bulk of the oil, lies above 300°. In any case the behaviour on boiling depends altogether upon the experimental conditions (shape and size of the flask, mode of fixing the thermometer, &c.) which explains,
among other things, why different investigators have in the past obtained different results).

Another serious error lies in the incorporation of the colour-reaction which was recommended at the time by Conrady for testing sandalwood oil. We have repeatedly pointed out that this reaction is quite useless for sandalwood oil evaluation.

Chemical Preparations and Drugs.

Aldehydes, Higher. It has been ascertained (chiefly in our laboratories), that the characteristic carriers of the odour of a large number of oils of the first practical importance in perfumery and in the manufacture of essences are a series of the so-called higher aldehydes. These aldehydes have been named after the number of carbon-atoms contained in them and among them the following have been found to occur in essential oils: octylaldehyde (with eight carbon-atoms, C₈) in lemon oil; nonylaldehyde, C₉, in German rose oil, Ceylon cinnamon oil, mandarin oil, orris root oil, and probably also in lemon oil; decylaldehyde, C₁₀, in sweet orange oil, lemongrass oil, mandarin oil, orris root oil, neroli oil, cassie flower oil; duodecylaldehyde or laurinaldehyde, C₁₂, in pine needle oil from Abies pectinata.

Although these aldehydes occur only in fractions of one per cent they are of very material importance in determining the odour of the oil. They all possess a marked odour peculiar to themselves, and generally of a refreshing, fatty-sweet character, somewhat varying, of course, in each member of the series. The particular shade of odour peculiar to each separate aldehyde only becomes perceptible in high dilution, as, for instance, in alcoholic solution.

We have now incorporated into our lists a series of these higher aldehydes, namely octylaldehyde, nonylaldehyde, decylaldehyde, undecylaldehyde, and duodecylaldehyde (laurinaldehyde). The applicability of the aldehydes may be inferred in part from their occurrence in the natural oils, as stated above, that is to say, they can be used in the first place in the preparation of the corresponding synthetic oils, such as sweet orange oil (decaldehyde), lemon oil (octyl- and nonylaldehyde), rose oil (nonylaldehyde) and so on. Further, according to recent experiments by leading French perfumers, some of the aldehydes in question will find a new field of usefulness in the preparation of fine perfumes. Duodecylaldehyde, in particular, when added to α-ionone in proportions of 5% or

2) Report October 1897, 54; April 1904, 82.
to \( \beta \)-ionone in proportions of \( 10\% \), is credited with imparting to violet-scent mixtures prepared with it their much-esteemed, refreshing, herb-like, so-called "green" aroma. A similar addition will serve to revive and thereby save such preparations as violet-extracts which, when made according to the usual recipes, have a flat and inexpressive odour. From another quarter the same aldehyde is recommended for scent of an orange-character, and also, in particular, to produce the effect of lily-of-the-valley.

It appears to us, however, that for oils of the Citrus species the lower aldehydes (decyl- or possibly undecylaldehyde) would be more suitable, especially for such scents as Eau-de-Cologne and others of that kind. Octylaldehyde is reported to be particularly adapted for scent mixtures of the character of "Jasmine rose", while nonylaldehyde, as already stated, is chiefly suitable for producing rose-like effects.

The aldehydes above referred to may perhaps be regarded as the most productive and subtle synthetic perfumes at present known. In accordance with these qualities they must be handled and stored with the greatest care. They are best kept in solutions of from 5 to \( 10\% \) in the purest alcohol and in dark, fully-filled bottles in a cool place. When measuring out the quantity to be added, the perfumer must bear in mind that only very small proportions may be used, say about \( 0,1\% \) for oils, a correspondingly larger proportion for terpeneless synthetic oils, and a correspondingly smaller one for extracts. As an over-dose is more likely to be harmful than an under-dose, the greatest care should be taken with the addition.

Undecyl- and duodecylaldehyde (laurinaldehyde) are only supplied by us in \( 10\% \) alcoholic solution, because of their very limited keeping-power.

We must expressly point out that we are not in a position to give more precise directions for the use of our new aldehydes and we therefore earnestly advise those who have not thoroughly mastered the art of fine perfumery in all its branches, to abstain from experimenting with these costly preparations, which require for their successful use a thoroughly trained sense of smell and complete familiarity with all the aids of modern perfumery.

**Benzyl Acetate, free from chlorine.** In the course of the past half-year inferior qualities of this ester (which, to be sure, had the doubtful advantage of being low-priced) have repeatedly been submitted for our opinion. As already pointed out in our last Report (p. 111) a preparation, to be of good quality, must contain from 98 to \( 100\% \) ester and must be free from chlorine-compounds. Neither condition was existent in the samples submitted to us, the ester-content falling as low as \( 91,5\% \).

**Benzyl Benzoate.** The recent examination of a sample of "cheap" benzyl benzoate proved once more that there is always a natural ex-
planation of such "cheap" prices. The sample submitted to us had the following characters: $d_{150} 1,1198$, $n_{D20} 1,56836$, ester-content 93,7%. Its inferior quality was revealed in the first place by the ester-content, which was much too low, the specific gravity and index of refraction being also below the mark. The product, furthermore, did not solidify below about 15,5°, whereas the solidifying point of a preparation which answers all requirements is about 18°. In determining the solidifying point it is necessary to cool down the oil to about $+10°$, as otherwise the process of solidification proceeds too slowly.

We desire to call attention to the necessity of always stipulating that benzyl benzoate, whatever the conditions, should have an ester-content of from 98 to 100%. The sp. gr. of a preparation of good quality lies between 1,121 and 1,125 and the index of refraction between 1,569 and 1,570 (20°).

**Borneol.** The Revue scientifique (1911, p. 82) contains an article on Borneo-camphor, which is here referred to in passing because we have on several occasions dealt with the principal subject-matter of the contribution, which is chiefly devoted to a description of the collection of the drug.

**Civet.** We cannot too frequently direct attention to our excellently assorted stock. At the present time a somewhat large shipment is on the way for us, and judging by the samples to hand, its quality may fairly be described as exquisite. We hope that it may not be necessary to alter our selling-prices, but the article is very firm indeed, the demand for really good qualities being quite keen.

**Menthol.** Generally speaking, adulteration of menthol is seldom heard of in the wholesale trade, and for that reason a recent experience of ours in connection with the delivery of a parcel of menthol may be of interest. When the residual mother-liquor after the first recrystallisation of the crude product was about to be again worked up for menthol, we obtained crystals which, although similar to menthol in appearance, had a much higher melting-point and contained a considerable proportion of halogens. After repeated recrystallisation from dilute alcohol they finally gave m. p. 76°. Our surmise that these crystals consisted of α-bromo-camphor was confirmed both by the pronounced halogen-reaction and by the fact that, when reduced with zinc-dust and glacial acetic acid, they could be converted into camphor; the last-named body being identified from its oxime and its semicarbazone.

Whether the adulteration had been practised in Japan or in England, where the parcel had been in warehouse for some considerable time, could

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1) Quoted from Annal. de Pharm. 17 (1911), 489.
2) Comp.: Report April 1905, 99; April 1907, 25; October 1910, 149; April 1911, 135.
not be discovered, but in any case we desire to call attention to a form of adulterant which will most probably again be found in menthol on several occasions, especially when menthol-prices are high.

We report on the market-position of menthol under peppermint oil, Japanese, p. 102.

**Musk, Tonquin.** For some considerable time the price-fluctuations of this important article have moved within a narrow compass. As may be imagined, the musk-trade in China has suffered severely during the last few months from the effects of the Revolution, and the supplies from the interior to Shanghai have been completely suspended. Nevertheless the market has not been affected in any way, and it may therefore be concluded that the stocks in the principal consuming countries were sufficient, and that this was the reason why the cessation of trade in the country of production has failed to make any impression.

**Exports of musk from Shanghai in the year 1911.**

<table>
<thead>
<tr>
<th>Year</th>
<th>to Paris</th>
<th>to London</th>
<th>to New York</th>
<th>to Germany and Austria</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1911</td>
<td>417</td>
<td>155</td>
<td>317</td>
<td>20</td>
<td>909</td>
</tr>
<tr>
<td></td>
<td>compared with</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1910</td>
<td>722</td>
<td>239</td>
<td>287</td>
<td>65</td>
<td>1313</td>
</tr>
<tr>
<td>1909</td>
<td>480</td>
<td>161</td>
<td>186</td>
<td>60</td>
<td>887</td>
</tr>
<tr>
<td>1908</td>
<td>666</td>
<td>37</td>
<td>211</td>
<td>9</td>
<td>923</td>
</tr>
<tr>
<td>1907</td>
<td>829</td>
<td>57</td>
<td>337</td>
<td>37</td>
<td>1260</td>
</tr>
</tbody>
</table>

**Peru Balsam.** In a critical review of the method for the determination of cinnamene in Peru balsam prescribed in the German Pharmacopœia Ed.V, F. Lehmann and A. Müller ¹ call attention to certain imperfections in the Pharmacopœia-prescription.

The first of these imperfections is that the volume of the cinnamene which has gone into solution is entirely disregarded in the calculation. If, as prescribed, 2.5 g. balsam is shaken up with 50 cc. ether and the necessary quantity of liquor, the ether layer, when the mixture has been left to settle, does not represent 50 cc., as is assumed in the Pharmacopœia-test, but 51 cc. This means that in following the Pharmacopœia-method over 1% cinnamene less is taken into account than is actually found present when the figures used represent the real conditions.

Stöcker ² had already called attention to another cause of error. He had discovered that when the alkaline ethereal balsam mixture is not shaken

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¹ Arch. der Pharm. 250 (1912), 1.
² Apotheker Ztg. 26 (1911), 283.
sufficiently long the cinnamamine-values are too low. This is confirmed by Lehmann and Müller, who have found that the best method of correcting this error is not to add the liquor until the balsam alone has been shaken with ether for some time.

The addition of tragacanth as a clarifier is much to be recommended, but a smaller quantity than that stated by Fromme (Annual Report of the firm of Caesar & Loretz, Halle a. S., 1909) will suffice. This agrees with our experience.

Lehmann and Müller regard it as preferable to carry out the entire cinnamamine-determination volumetrically, and for this purpose they give the following prescription: —

To 2.5 g. Peru balsam add 5 g. water, shake, add a weighed quantity of 30 g. ether and shake the mixture for one minute. Add 5 g. soda liquor, again shake for 1 minute, leave standing for about 10 minutes and then carefully pour off the layer of water until only about 3 cc. is left. Next add 0.5 tragacanth and shake vigorously. After from 3 to 5 minutes, pour the principal quantity of the ether-solution (25 to 28 g.) into a wide-necked small flask, which, together with the cover, has been carefully tared, and determine the weight of the ether-solution. When the ether has evaporated in the water-bath the viscous cinnamamine residue is dried for from 30 to 45 minutes at about 100°, allowed to cool in the desiccator and weighed.

If, with 2.5 g. Peru balsam and 30 g. ether, the quantity of ethereal cinnamamine solution used up in the experiment equals \( a \) grams, and if, after evaporation of the ether, these are found to have yielded \( b \) grams cinnamamine, the percentage of cinnamamine-content in the Peru balsam is ascertainable by the following formula: —

\[
\frac{1200 \cdot b}{a - b}
\]

We may further state, although the fact is self-evident, that when a cinnamamine-estimation is carried out according to the German Pharmacopoeia, Ed. V, care should be taken that the temperature throughout the experiment is as equal as possible, as the volume of the ether-layer is subject to fairly considerable changes as a result of alterations in temperature.

Pollantin. As stated in our last Report (p. 114), our new Pollantin salve has been favourably received by the great majority of patients to whom we have sent samples with a request to give the article a trial. According to medical reports the percentage of patients whose condition was considerably ameliorated by the use of this ointment was 53, that of patients showing a partial improvement 32, and that of patients who failed to obtain relief from the remedy 15. The new preparation, which is supplied in the same manner as are our other Pollantin-preparations, has been
placed upon the market in the hope that it will bring relief to many hay-fever patients who, in spite of all precautions, were unable to obtain really good results from the previously available Pollantin-preparations.

After prolonged experiments Prof. Dunbar has been successful in discovering an effective mode of administering Pollantin as a remedy in the exceedingly troublesome form of asthma which afflicts certain patients in the later stages of hay-fever. His process consists in compressing the finest sifted Pollantin-powder, together with sugar of milk and a suitable binding-material, in the form of tablets, which are slowly dissolved in the mouth. Numerous patients to whom we have sent samples of the remedy for trial report that the tablets have afforded them the desired relief, but before we place the preparation upon the market we desire to collect further opinions, and we shall be pleased to place experimental samples at the disposal of the medical profession, and to receive reports on their therapeutic action.

We desire once more to inform our customers, and in particular the pharmacists among them, that we are prepared to receive old tins of liquid Pollantin bearing control numbers below 153 in exchange for fresh serum, and we therefore request them to look out such numbers, if any, from their stocks, and to send them to our Branch Office. Upon receipt the new tins will be forwarded by return. In reply to numerous enquiries we may add that, as powdered Pollantin has unlimited keeping quality, it cannot be exchanged.

Rose "Schimmel & Co." (Red Rose). The success of this speciality exceeds our highest expectations. We are able to say without exaggeration that no novelty of the past decade has been received by the manufacturing perfumery-trade with anything like the acclamation which has been bestowed upon this article: our sales-book is the best witness of this assertion. The extension of our rose-plantations which has been carried out last autumn was mainly determined by our growing requirements of the natural rose-extract, which, as is well-known, forms the basis of the preparation, and to which the manufactured article is chiefly indebted for its excellence. It is to be hoped that last year's crop-failure will be followed, this season, by a normal output, so that we may be in a position to prepare enough to meet the demand.

Safrol. When, in the course of last summer, the large supplies of camphor oil received by us had been for the greater part used up, we were able to reduce the price of safrol somewhat. After this we concluded most important contracts for delivery, which shows once more that our manufacturing capacity is planned on a scale which enables us to meet all competition at home or abroad. As always, the United States has been the principal consumer, considerable quantities of safrol finding a market in that country for all manner of purposes. In view of the general
condition of the artificial perfume industry we regard it as improbable that there will be any need for reducing the price to a material extent within the next few months.

**Thymol.** The trade in this article has been unable to recover from the senseless competition which has ruined it. Since our last Report the prices of ajowan-seed have become somewhat firmer, but in spite of this it is impossible to bring about a corresponding rise in the quotations for thymol, because some of the principal producers, calculating the price of the manufactured article on the basis of the cheap raw material prevailing some time ago, are determined to underbid. It is fortunate that our branch of industry offers no other similar example of mutual "freezing-out", and it must be a matter for surprise that the Hamburg manufacturers, who are the parties most concerned, have not yet grown tired of continuing this preposterous competitive fight. Speaking for ourselves, we have no difficulty in disposing of our make at our own prices.
Notes on Scientific Research in the Domain of the Essential Oils.

General.

In a treatise by Alice Henkel 1) on American medicinal plants we find some data on the habitat of numerous plants which are used in the manufacture of essential oils. Wintergreen (Gaultheria procumbens, L.) occurs on sandy spots in cool, damp woods, and especially underneath evergreen trees in Canada and the North-Eastern States of the Union. Catnip (Nepeta Cataria, L.) which was imported from Europe, now grows throughout North America, from Canada and Minnesota in the North to Virginia and Arkansas in the South. The geographical distribution of pennyroyal extends from Nova Scotia and Quebec in the North to Dakota in the South. Bugleweed (Lycopus virginicus, L.) is found from Canada to Florida, Missouri and Nebraska. Peppermint (Mentha piperita, L.), an importation from Europe, occurs from Nova Scotia and Minnesota in the North to Florida and Tennessee in the South. The boundaries of the geographical distribution of spearmint (Mentha viridis, L.) a plant which has also been brought over from Europe, are Nova Scotia, Utah and Florida. Canada Fleabane (Erigeron canadensis, L.) inhabits the greater part of North America. The Yarrow (Achillea Millefolium, L.) extends from New England to Missouri. Tansy (Tanacetum vulgare, L.) has been carried over from Europe to America and is now found from New England and Minnesota as far as North Carolina and Missouri, Wormwood (Artemisia Absinthium, L.) is also a native of Europe; it inhabits the North Western part of the United States from Newfoundland to New York. Fireweed (Erechthitis hieracifolia, Raf.) has a geographical distribution extending from Canada to Louisiana and Nebraska.

On p. 147 of our Report of April 1911 we referred to the experiments in the cultivation of medicinal plants which are being carried on in Austria by W. Mitlacher. Further information on this subject is given in a reprint from the Zeitschrift f. d. landwirtschaftliche Versuchswesen in Österreich, 1911, of which a copy has been kindly sent to us by the author.

Sachsse & Co. 2) have investigated the influence of peroxide of hydrogen upon agents for correcting the taste of mouth-washes. They admixed 0,05 g. of the essential oil under examination to a mixture of 40 g. alcohol (90% by vol.), 30 g. water and 25 g. peroxide of hydrogen (12%). After standing for one to two months the taste of this mixture was compared with that

2) Apotheker Ztg. 27 (1912), 19.
of a precisely similar freshly-prepared mixture. It was found that peroxide of hydrogen causes a pronounced alteration in geraniol, menthol, menthyl acetate, peppermint oil, and cinnamic aldehyde; that it effects a less pronounced change in carvacrol, eugeno1, geranium oils, clove oil and terpineol, and that it leaves unaffected anethol, Russian anise oil, bornyl acetate, eucalyptus oil, Siberian pine-needle oil, star anise oil, and thymol.

Bibliography.

Those who desire to acquire a knowledge of the nature of refraction, as well as of the coefficient of refraction (the latter being an important factor in the examination of the separate constituents of essential oils) will find in the Refraktometrisches Hilfsbuch lately published by Veit & Co., Leipzig (1911), an excellent guide. In the introduction to the work, the authors, Prof. Dr. W. A. Roth and Dr. F. Eisenlohr, who are known by their researches in the domain of the determination of chemical constitution by physical means¹ explain the meaning of the terms "coefficient of refraction" and "molecular refraction", after which they deal with dispersion and its cause. In the following chapters they treat of the principles of refractometry and describe in detail the various refractometers. An important section of the book consists of chapters on the development of molecular refraction and dispersion as well as on exaltation and specific exaltation. Want of space forbids us from entering into details on the abundance of interesting material in the book, but we cannot omit to mention that it contains an exact guide to the determination of specific gravity by means of various pycnometers and at different temperatures as well as many tables, including logarithm-tables up to the fifth decimal, which greatly facilitate calculations.

Analytical Notes.

The passage in our Report of October 1911 (p. 119) relating to J. Herzog's suggestions on the subject of the test for chlorine compounds in benzaldehyde has caused that author to make a reply²) in which he again lays stress upon the advantages of the modification proposed by him, and in which he leaves it to his fellow-chemists whether they will adopt his method or ours.

G. Heyl³) and E. Rupp⁴) have also intervened in the discussion of this subject. Heyl recommends the lime-test for chlorine, which he carries out as follows:

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²) Berichte d. deutsch. pharm. Ges. 21 (1911), 536.
³) Apotheker Ztg. 27 (1912), 49.
⁴) Ibidem 92.
1 to 2 gr. chlorine-free hydrate of lime are stirred up with a glass rod in a small porcelain dish with 10 to 15 drops benzaldehyde, the mixture is then covered with a thin layer of hydrate of lime and slowly brought to a red heat. After cooling the contents of the dish are poured into a beaker, 5 to 6 cc. water are carefully added, and the mixture is faintly acidulated with nitric acid. The solution is then filtered through chlorine-free filtering paper or glass-wool and is tested for chlorine with silver nitrate.

By this method Heyl was able to trace clearly so small a proportion of chlorine as 1 drop of monochloro-benzene in 50 gr. benzaldehyde.

Rupp proposes for the same purpose the copper oxide test (the so-called Beilstein test) for which he gives the following modus operandi: —

A copper wire, or, better still, a strip of copper wire-netting 0,5 cm. in width (about 1 mm. mesh) is twisted at one end into a narrow spiral shape, forming a roll about the diameter of a large pea. This roll is repeatedly drawn through a non-luminous flame in order to oxidise the surface of the copper and to remove any yellow or green coloration. When cooled, the roll is dipped into the benzaldehyde under examination and is then exposed to the flame for a moment in order to inflame the benzaldehyde. When the benzaldehyde is burnt off (not in the flame) the roll is again applied to the top of the flame. If there is a green inflammation, chlorine is present.

A roll of netting absorbs about 0,3 gr. and a wire-spiral about 0,1 gr. of the substance to be tested. Rupp found that when a roll of wire netting was used, so small a mixture as 1 drop benzylchloride in 50 gr. benzaldehyde gave a clearly perceptible reaction, whereas with copper-wire a mixture of 50 gr. benzaldehyde and 2 drops of benzylchloride was needed to produce such a reaction.

We ourselves have also suggested both these methods for the detection of chlorine in essential oils and preparations¹, but notwithstanding this we prefer the combustion method for the purpose here under discussion, that method having been specially worked out for the testing of bitter almond oil for chlorine. Our experience shows it to be superior to the lime-test (although in itself that test is a sensitive one), inasmuch as it can be carried out more rapidly, especially when a series of oils is to be tested. And where minute proportions of chlorine are concerned, the copper test is decidedly inferior to both the combustion and the lime-methods, not only in respect of sensitiveness, but especially in respect of certainty of action. Hence the copper test can only be recommended under reserve and for the purposes of a preliminary examination.

In our last Report (p. 121) we mentioned a paper by Fuller, in which he recommended Walther's hydroxylamine method (Report April 1900, 22) for estimating the camphor-content of spirits of camphor. E. K. Nelson has now investigated the general applicability of this method to ketones, and has found it to give tolerably satisfactory results with carvone, pulegone, camphor, thujone, and menthone. He therefore regards it as suitable for the quantitative estimation of the ketones in question, especially in cases where these ketones constitute the principal portion of an oil. But in the case of oils in which the ketones occur only as constituents of secondary importance it is necessary to make further special investigations to determine how the other constituents behave when attacked by the reagent.

Several determinations made by Nelson with various oils have given the following results:

<table>
<thead>
<tr>
<th>Oil</th>
<th>Carvone (°/o)</th>
<th>Thujone (°/o)</th>
<th>Pulegone (°/o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spearmint oil</td>
<td>58,4</td>
<td>53,1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>65,5</td>
<td>66,4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>61,4</td>
<td>60,7</td>
<td></td>
</tr>
<tr>
<td>Tansy oil</td>
<td>68,6</td>
<td>65,4</td>
<td></td>
</tr>
<tr>
<td>Wormwood oil</td>
<td>33,2</td>
<td>31,2</td>
<td></td>
</tr>
<tr>
<td>Pennyroyal oil</td>
<td>81,9</td>
<td>—</td>
<td>6% pulegone</td>
</tr>
<tr>
<td>Rosemary oil</td>
<td>30,3</td>
<td>30,2</td>
<td>camphor</td>
</tr>
</tbody>
</table>

Experiments made by Nelson with fenchone showed the quantitative estimation of that body to be impossible by Walther's method.

Judging from our own present experience with this method our attitude towards Nelson's optimistic views is somewhat sceptical, but we are not prepared to express a definite view on the matter. In commenting upon Fuller's article at the time (Report October 1911, 121) we stated that a control-test made by us for determining the camphor-content of spirits of camphor had failed to give satisfactory results.

In our October Report of 1910, p. 139, we mentioned the method for testing turpentine oil which has been worked out by Louise, and which is based upon the miscibility of this oil with aniline, and the determination of the so-called curve of miscibility. The same author has recently applied the same principle to the examination of lavender oil, neroli oil, lemon oil, peppermint oil, sandalwood oil and copaiba balsam oil. It would appear that by plotting a miscibility-curve it is possible to discover adulteration in oils of lavender and neroli and to differentiate between French, Japanese and American peppermint oils.

1) Published also as Circular No. 77 of the Bureau of Chemistry, U. S. Dept. of Agriculture.
3) Journ. de Pharm. et Chim. VII. 4 (1911), 194.
Methods for the determination of citral in lemon oil are described on p. 75.

On the determination of the number of ethylene linkings in hydroaromatic bodies, see Chemical Notes, p. 165.

**Physical Notes.**

We have before us for comment several interesting papers by A. Golodetz.

1. "On new methods for the separation of mixtures with closely-approximating boiling-points, and of mixtures which boil without decomposition". For the purpose of separating mixtures of liquids the author availed himself of the property of many mixtures of distilling at a temperature, lower than the boiling-temperature of the pure components of the mixture. To a binary solution distilled at minimum boiling-point, which therefore cannot be completely separated by fractional distillation, Golodetz adds a third body which also boils at minimum boiling-point with one of the components of the mixture, and at a temperature which must be lower than that of the binary mixture. Toluene, for example, boils at 110,4°, acetic acid at 118°. Now, if a mixture in any proportion of these two liquids is distilled, there passes over at 104° a distillate which is always composed of 31,9% by weight of acetic acid and 68,1% toluene, and upon increasing the distilling-temperature there distils over the liquid which was present in excess of the mixture-proportion mentioned above. Separation by fractional distillation is therefore impossible by this method. It can be accomplished, nevertheless, when to the mixture a third body is added which distils over at minimum boiling point with one of the two other components of the mixture; that is to say, with the acetic acid if it is desired to keep back the pure toluene in the evaporation, or with the toluene if it is desired to keep back and gain the pure acetic acid. Such bodies are, in the first place benzene, in the second, water.

The author now made the following experiment: he mixed 68,1 g. toluene with 31,9 g. acetic acid and, in order to be able to distil off the acetic acid in the receiver, and to obtain the toluene in the pure form, added a quantity of benzene corresponding to the composition of the steam when benzene and acetic acid distil over together at minimum boiling-point. In the present case this quantity was rather large (1800 g.), for at minimum boiling point the mixture only contains 2% acetic acid to 98% benzene. Golodetz distilled the entire mixture in a still with a fractionating-head and obtained in the last fraction 46,1 g. pure toluene, = 67,5% of the total quantity employed.

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The following experiments in separation were carried out in a similar manner:

To a mixture of 127 g. acetic acid and 274,4 g. toluene Golodetz added 67 g. water (minimum boiling point of the mixture of water and toluene 81,4°, proportion 19,6% water). Fractional distillation gave for the highest boiling fraction 64 g. pure acetic acid = 50,2% of the quantity present in the mixture.

242 g. toluene mixed with 60 g. benzene were diluted with 39,5 g. methyl alcohol (b. p. 64,7°) (minimum boiling point of the mixture of methyl alcohol and benzene 58,35°; proportion 60,45% benzene). After fractional distillation 228,5 g. pure toluene was obtained.

Also:

\[
\begin{align*}
36,3 \text{ g. benzene, b. p.} & \quad 80° \\
23,7 \text{ g. methyl alcohol, b. p.} & \quad 64,7° \\
170 \text{ g. carbon disulphide, b. p.} & \quad 46°
\end{align*}
\]

Result: 23 g. pure benzene = 63,4%.

Also:

\[
\begin{align*}
45 \text{ g. ethyl butyrate, b. p.} & \quad 119,9° \\
15 \text{ g. amyl bromide, b. p.} & \quad 118,5 \text{ to } 119° \\
39 \text{ g. } n\text{-propyl alcohol, b. p.} & \quad 97,2°
\end{align*}
\]

Result: 30 g. ethyl butyrate = 66,7%.

The experiments mentioned by the author are only intended to explain the method; it is not claimed that they are all of practical usefulness.

The method of separation by distilling, making use of the minimum b. p., was known1). But to Golodetz belongs the merit of having again illustrated by striking examples this property of numerous mixtures which is so little used in practice.

At the conclusion of his paper the author states "from all the above experiments it is evident that the mixtures which boil without decomposition behave like uniform chemical entities; a fact which has already been pointed out by Makowiecki."

The fact that a distilled solution possesses a constant temperature and a constant composition of steam does not of itself warrant the conclusion that it represents a chemical compound. It is only when the boiling point is also a maximum boiling-point that the presence of a molecular chemical compound may be assumed with certainty. The only exception to this rule which is at present known is a solution of formic acid in water which, although the melting-point curve shows a maximum b. p.,

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nevertheless forms no compound. But an additive compound which has a lower b. p. and at the same time a higher steam-pressure than its components is scarcely imaginable, and as a matter of fact has not yet been discovered. Probably the true explanation of the homogenous mixtures with minimum boiling point is to be found rather in conceiving them as transition-members between the heterogenous mixtures and the solutions proper. From an optical standpoint it is true that they are solutions, but for the rest their minimum boiling-point connects them more nearly with the mixtures of mutually insoluble or sparingly soluble substances.

2. “On fractional distillation in the laboratory and on new rectifying apparatus”

A. Golodetz here deals with the course of the process of fractional distillation of mixtures and with the conditions which should govern the construction of distilling-apparatus for laboratory use. He begins by explaining the familiar forms of such apparatus and then proceeds to explain a new model of fractionating-head, which he calls the “birectifier”. We reproduce below the result of a trial distillation with this apparatus. The charge consisted of equal parts of benzene and toluene, and the steam-pressure was 746.5 mm.

<table>
<thead>
<tr>
<th>Temp.-Interval</th>
<th>Quantity of Distillate</th>
</tr>
</thead>
<tbody>
<tr>
<td>79.42 to 79.6°</td>
<td>42%</td>
</tr>
<tr>
<td>79.6</td>
<td>3.95%</td>
</tr>
<tr>
<td>80.4</td>
<td>1.7%</td>
</tr>
<tr>
<td>81.4</td>
<td>0.8%</td>
</tr>
<tr>
<td>83.4</td>
<td>0.45%</td>
</tr>
<tr>
<td>86.4</td>
<td>0.35%</td>
</tr>
<tr>
<td>89.4</td>
<td>0.43%</td>
</tr>
<tr>
<td>95.0</td>
<td>0.72%</td>
</tr>
<tr>
<td>100.5</td>
<td>0.95%</td>
</tr>
<tr>
<td>103.5</td>
<td>0.98%</td>
</tr>
<tr>
<td>106.5</td>
<td>2.85%</td>
</tr>
<tr>
<td>109.3</td>
<td>4.25%</td>
</tr>
</tbody>
</table>

Toluene (from the difference) 40.85%.

The first and the last fraction might be regarded respectively as almost pure benzene and toluene.

For purposes of comparison the author has distilled quantities of 100 g. each of a single sample of turpentine oil in his own and in six other distilling-heads. In the details of these experiments no mention is made of the pressure, and whether in all the experiments it was precisely, and not only approximately the same. The action of a fractionating apparatus depends in the first place upon the pressure.

1) Chem. Industrie 35 (1911), 102 and 141.
3. "On new methods for the separation of mixtures of liquids of which the boiling-points are the same, or lie close together"). This paper is the first of a series of articles which apparently treats the subjects just referred to in greater detail. We intend to deal with this matter when the series is completed.

4. "On fractional distillation with steam"). A Golodetz has carried out several distilling-experiments with the object of discovering whether it is easier to separate a mixture of liquids with different degrees of volatility by means of distillation with water or by dry distillation. He obtained the following results: —

"a) Fractional distillation of mixtures of substances insoluble in water, and water (provided the b. p. be not too high), gives excellent results, much better than those obtained by ordinary distillation under similar conditions.

b) The distillation of mixtures of high b. p. gives less satisfactory results, but when high rectifying apparatus is employed, distillation with water also answers very well in this case.

c) In the course of the rectification-process the mixture distilled with water undergoes certain changes consisting in the simultaneous alteration of temperature and pressure, which changes proceed in different directions.

d) The process of distillation is completely governed by Young's law, according to which the quantity of liquid which has been distilled off in the presence of water up to the mean of the difference in temperature between the boiling-points of each component part, equals in quantity the whole of the first component, plus the corresponding quantity of water.

e) The result of the fractionation depends upon the difference between the boiling points of the individual components with water, and upon the quality of the rectifying apparatus."

Apart from conclusions b and d, the other statements are incorrect. The author has made too light of his task. He makes two experiments in fractionation with a mixture of benzene-toluene and water, and then compares the results of this distillation with water with the results of an experiment in dry distillation made by another author. The separation in the said author's experiment having given less favourable results than in his own, Golodetz concludes that fractionation of the oil-mixture with water is the better method. In arriving at this conclusion, he happens to have hit upon a rather poor experiment in separation among those recorded in literature. Thus, for example, Young's distilling-experiments")

1) Chem. Ztg. 36 (1912), 273, 297.
2) Zeitschr. f. physik. Chem. 78 (1912), 641.
have given better results for fractionation without the aid of water as an evaporating-agent. Golodetz should have made the comparative test himself, using the same fractionating-head, and with the same rate of speed in distilling, and the same distilling temperature. For the separation of a mixture of vapours also depends, among other things, upon the extent of the partial condensation in the fractionating-head. In the well-known forms of fractionating-heads, as used in laboratory-work, and also in his own "birectificator", there takes place a process known as "wild dephelegmation", i.e. a process of condensing induced by the cooler outer air which defies regulation, and, this being so, the degree of steam-temperature, given equal heating, is also a factor in determining the measure of separation.

The other distilling-experiments of Golodetz also fail to bear out his assertion that fractional distillation with water yields better results than does ordinary distillation. He distilled a mixture of amyl formiate and amyl acetate with water, and obtained an excellent separation-effect, but he has not made any comparative distilling-experiment without water.

On p. 641 of his treatise the author states that fractional distillation by steam is quite a recent practice in essential oil chemistry. This assertion would be correct if he had added the words "in the public laboratories", for this mode of fractionation has been in use in the essential oil industry for the past half century or so.

In the course of our numerous comparative experiments, some of which have been published¹), we have found that where the separation of homogenous mixture of liquids is concerned, distillation by water is less effective than dry distillation in cases where the mixture is not at all or only slightly soluble in water. But where one of the components of the mixture is soluble in water, that component is impeded, in water-distillation, in proportion to its degree of solubility in the evolution of steam. The component being thus kept back during the process, water-distillation in this particular instance gives an excellent fractionation, in particular when carried out with a fractionating-head.

In the process of water-distillation of mixtures of liquids which are not soluble in water to any extent, the steam only participates in the formation of vapour to this extent that, while it is passing through, an oil-free space is created into which the oil-mixture immediately commences to pour its vapour, until saturation-point has been reached. The steam determines the extent of the generation of vapour from the oil-mixture, but it does not influence the percentage of the oil-vapour. This is precisely the same as that of the saturated oil-vapour which rises from the same oil-mixture at the same temperature when no water is present.

It may be said that steam, just as air or other indifferent gases, when used as an evaporating-agent, plays the part of an air-pump.

In theory, therefore, water-distillation should be able to separate a mixture of liquids insoluble in water just as readily as is done by distillation without water at the same steam-temperature. But in practice it is found, *ceteris paribus*, that the separation-effect obtained with water-distillation is not so good, because when a fractionating head (or, in working on a large scale, a column) is used, the exchange of the vapour mixture with the condensate (which is the determining factor when fractionating the oil-vapour), is disturbed and impeded by the quantities of water which are admixed with the oil and which in some cases overlay it. This is the reason why low-boiling mixtures of liquids are more readily separated by water-distillation than are less volatile mixtures: a fact which has also been observed by Golodetz. For in the case of the first-named mixtures the condensed steam contains comparatively little water, but in the case of the latter it contains a great deal. For example, 1 kilo steam, when boiling takes place at atmospheric pressure, is capable of evaporating 9,11 kilos benzene or 5,82 kilos toluene, but only 0,18 kilos nitrobenzene or 0,05 kilos naphthalene.

Our Report of October 1910 contained a paragraph (p. 167) relating to a paper by Auwers and Roth on the thermic value of various terpene-bodies. Soon after the publication of this paper the authors' attention was drawn to a slight experimental error, owing to which the ascertained values had been slightly below the actual. Auwers, Roth and Eisenlohr¹, however, have found that the theoretical conclusions which they had drawn from their previous experiments are in no way affected by the increase of the separate values.

A paper by Auwers and Moosbrugger²) on the refraction and dispersion of organic substances³) with several double linkings contains data concerning the dispersion and refraction-values of a series of alicyclic diënes⁴) and other oxygenated compounds of an analogous constitution. The commonly accepted theory that all these compounds are spectrochemically normal is in essence based upon conclusions of analogy which rest upon a very weak experimental foundation.

Examined spectrochemically the bodies under review showed no tendency towards exaltation either in their index of refraction or of dispersion.

¹) Liebig's Annalen 385 (1911), 102.
²) Liebig's Annalen 387 (1912), 167.
⁴) Diënes, according to the Geneva nomenclature, are hydrocarbons with 2 double bonds.
A study of the data observed by the authors shows that neither the boiling point nor the density of an alicyclic diène affords any guide as to whether the body is one with conjugated or with isolated double linkings. Determination of the refractive index also is of little value. But by calculating the molecular refraction or dispersion, and by applying the values thus obtained in the testing of the preparations, much better results are afforded. Compensation of antagonistically active influences could only occur in cases where an acyclic diène without conjugation contained at the same time admixtures of a diène with conjugated double linkings and of a cyclic isomeric diène.

In order to prepare pure acyclic diènes, Auwers and Moosbrugger heated the unsaturated carbinoles with bisulphate of potassium, a manipulation in which it is essential to remove the hydrocarbon which is generated as quickly as possible from the reaction-mixture. To achieve this object the best plan is to heat the alcohol and the sulphate under diminished pressure, while simultaneously passing dry hydrogen through the mixture.

Among other bodies, the authors have spectrochemically examined geraniolene (from geranic acid and from dimethyl heptenol), 2,6-dimethyl-octene-2-ol-6 (from methylheptenone and magnesium ethyl iodide)\(^1\), \(\alpha\)- and \(\beta\)-cyclogeraniolene and homolinalool (2,6-dimethyl nonadiene-2,8-ol-6).

Auwers has also, in collaboration with Ph. Ellinger\(^2\), investigated the problem of differentiating between hydroaromatic bodies with endocyclic and with semicyclic double linkings. Wallach’s discovery that a semicyclic double linking regularly increases the molecular refraction above the normal value was of special importance in the identification of methene derivatives. It also appeared to be desirable to ascertain the normal value of the specific exaltation which occurs in methene hydrocarbons and to compare it with the exaltation values of the several varieties of conjugated systems.

The authors have re-calculated the observation-material collected by Wallach, using the densities compared with water at \(4^\circ\), as well as the exact molecular weights and the atomic refractions determined by Eisenlohr\(^3\). Generally speaking, the values for \(E\Sigma_d\) deviated in only a few cases by more than \(\pm 0.1\) from the ascertained mean; hence there was no occasion for determining the refractive index of other methene hydrocarbons, but it was necessary to discover whether these bodies also possessed an increased power of dispersion.

As was to be expected, the endocyclically saturated compounds not only exhibit a normal refraction, but also a normal dispersion and the moderate rise of the co-efficient of \(\Sigma\)refraction in bodies with a semi-

\(^1\) See p. 177.
\(^2\) Liebigs Annalen 887 (1912), 200.
\(^3\) Comp. Report April 1911, 155.
cyclic double linking corresponds with a clearly perceptible exaltation in the power of dispersion. The latter, however, is small and almost lies within the limits of error.

It is therefore possible to distinguish with clearness by the spectrochemical method between alkylcyclohexenes and alkylidene cyclohexanes.

In chemical literature a whole series of hydrocarbons is erroneously described as alkylidene cyclohexane derivatives, which in reality consists of endocyclically unsaturated compounds. Among these bodies, for example, are several hydrocarbons prepared by Sabatier and Mailhe.\(^1\)

Finally, Auwers and Ellinger have investigated the cyclohexenyl acetic acids and the isomeric cyclohexylidene acetic acids, and in particular the esters of these bodies, with the result that they have found that in them there is a marked difference between the compounds with semicyclic double linking and the endocyclic non-saturated isomerides. The latter are in every respect normal, but the former display pronounced exaltation in their coefficient of refraction, and still more pronounced exaltation in their power of dispersion. The reason of this is obvious, inasmuch as the cyclohexylidene acetic acids not only possess a semicyclic double linking but also a conjugation, and the first effect of the latter is a powerful rise in refraction and dispersion.

As many of the free acids with semicyclic double linking have high melting points it is advisable to use the esters for optical examinations.

Hantzsch \(^3\) calls attention to another physical property, namely absorption of the ultra-violet rays, which is of great importance in testing the purity of terpenes. Hantzsch has examined \(\alpha\)-pinene, \(d\)-, \(l\)-\(^3\) and \(i\)-limonene, dipentene, \(l\)-\(\alpha\)-phellandrene, \(\beta\)-phellandrene, sylvestrene, caryophyllene, \(m\)- and \(p\)-cymene, \(d\)- and \(l\)-camphor, and \(d\)- and \(l\)-borneol. All these bodies (of which the experimental material had been placed by us at the disposal of the author), were purified by Hantzsch by fractionation, using a glass-bead column, in a Claisen flask in a current of carbonic acid gas at 10 to 15 mm., from a bath of Wood's metal. The solutions required for the determination of the ultra-violet absorption were prepared with optically pure ethyl alcohol; in order to obviate oxidation it is necessary to pipette the freshly-prepared distillates in measuring-flasks which have previously been filled with carbonic acid. Hantzsch does not give the constants of the bodies examined by him, which is to be regretted, because they would have made it possible to ascertain in how far the properties of the preparations in question are influenced by impurities. In the examination of terpenes distilled in vacuo it soon became evident that the absorption-method is much more sensitive than the refraction-method,

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\(^1\) Compt. rend. 139 (1904), 343.
\(^2\) Berl. Berichte 45 (1912), 553.
\(^3\) In his paper, Hantzsch erroneously speaks of \(i\)-limonene as being prepared from orange oil. As a matter of fact, this terpene occurs in pine-needle oil.
inasmuch as such slight differences in the distilling-temperature as $1/10\degree$ were perceptible in the shape and position of the absorption-curve. The curves of the preparations under examination have been plotted by Hantzsch in several tables, in which on the vertical lines he gives the logarithms of the layers in mm., corresponding to $1/1000$ normal solutions, and on the horizontal line the oscillation-figures in the ultra-violet rays. The absorption increases in proportion to the nearness of the double-linkings. It is weakest in pinene with the bridge-linking and in limonene with the greatest distance of two double-linkings; it increases in strength as the double-linkings draw nearer together (as in sylvestrene), and it reaches its maximum in the conjugated linkings, conjugation outside the ring ($\beta$-phellandrene) being more active than that within the ring ($\alpha$-phellandrene).

A paper by J. F. Eijkman$^1$ on the refractometric behaviour of a series of organic bodies contains particulars of the refraction and density of certain terpene-bodies:

<table>
<thead>
<tr>
<th>Formula</th>
<th>t</th>
<th>d</th>
<th>$n_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulegane</td>
<td>C$<em>6$H$</em>{18}$</td>
<td>15,2</td>
<td>0,7799</td>
</tr>
<tr>
<td>Pinic acid</td>
<td>C$<em>9$H$</em>{14}$O$_4$</td>
<td>109,4</td>
<td>1,0925</td>
</tr>
<tr>
<td>$l$-Pinonic acid</td>
<td>C$<em>{10}$H$</em>{18}$O$_3$</td>
<td>110,7</td>
<td>1,0257</td>
</tr>
<tr>
<td>$\alpha$-Pinonic acid</td>
<td>C$<em>{10}$H$</em>{16}$O$_3$</td>
<td>109,1</td>
<td>0,9975</td>
</tr>
<tr>
<td>$\alpha$-Thujaketonic acid</td>
<td>C$<em>{10}$H$</em>{16}$O$_3$</td>
<td>79,6</td>
<td>1,0115</td>
</tr>
<tr>
<td>Pulegenic acid</td>
<td>C$<em>{10}$H$</em>{16}$O$_3$</td>
<td>17,5</td>
<td>1,0035</td>
</tr>
<tr>
<td>Puleganic acid</td>
<td>C$<em>{10}$H$</em>{18}$O$_2$</td>
<td>20,2</td>
<td>0,9618</td>
</tr>
<tr>
<td>Ethyl puleganate</td>
<td>C$<em>{12}$H$</em>{22}$O$_2$</td>
<td>11,8</td>
<td>0,9178</td>
</tr>
<tr>
<td>Pulegano nitrile</td>
<td>C$<em>{10}$H$</em>{17}$N</td>
<td>16,2</td>
<td>0,8814</td>
</tr>
<tr>
<td>Pulegano lactone</td>
<td>C$<em>{10}$H$</em>{16}$O$_2$</td>
<td>21,0</td>
<td>1,0146</td>
</tr>
<tr>
<td>$\Delta^4$-$\alpha$-Menthenol-1</td>
<td>C$<em>{10}$H$</em>{18}$O</td>
<td>80,0</td>
<td>0,8948</td>
</tr>
<tr>
<td>$\Delta^8$-$\alpha$-Menthenol-1</td>
<td>C$<em>{10}$H$</em>{18}$O</td>
<td>79,8</td>
<td>0,8703</td>
</tr>
<tr>
<td>Fenchone</td>
<td>C$<em>{10}$H$</em>{16}$O</td>
<td>14,5</td>
<td>0,9488</td>
</tr>
<tr>
<td>$\alpha$-Fencholenic amide</td>
<td>C$<em>{10}$H$</em>{17}$ON</td>
<td>117,9</td>
<td>0,9331</td>
</tr>
<tr>
<td>$\beta$-Fencholic acid</td>
<td>C$<em>{10}$H$</em>{16}$O$_2$</td>
<td>76,1</td>
<td>0,9638</td>
</tr>
<tr>
<td>$\beta$-Fencholic acid amide</td>
<td>C$<em>{11}$H$</em>{19}$ON</td>
<td>108,2</td>
<td>0,9072</td>
</tr>
<tr>
<td>$\beta$-Fencholic acid</td>
<td>C$<em>{10}$H$</em>{18}$O$_2$</td>
<td>18,9</td>
<td>0,9698</td>
</tr>
</tbody>
</table>

G. Ciamiciam and P. Silber$^3$), in their twelfth paper on the chemical action of light$^3$), describe the effect of light upon toluene, $\rho$-, $m$-, and $\sigma$-xylene, $p$-cymene, phenanthrene, and $p$- and $\sigma$-nitrotoluene. The $p$-cymene

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$^2$) Comp. Report October 1907, 123; October 1909, 159; October 1911, 122.

$^3$) Berl. Berichte 45 (1912), 38.
was exposed to light from June 13., 1911 to November 13., 1911 in 5 bottles, each of 1 litre capacity, filled with oxygen. Each bottle contained 15 grams cymene and 100 cc. water. When the bottles were opened a considerable vacuum was found, which had been caused by the consumption of oxygen. The reaction-liquid, which gave an acid reaction, was found to contain \( p \)-cuminic acid (m. p. 119°), methovinyl benzoic acid (m. p. 165°), and \( p \)-\( \alpha \)-hydroxy\( \beta \)-isopropyl benzoic acid. Experiments carried on in the dark showed no auto-oxidation.

**Pharmacop-physiological Notes.**

In a lecture by H. Emde\(^4\) it is stated that the chemistry of the essential oils affords many examples of Loew’s well-known law that bodies with double bonds are more poisonous than the corresponding saturated bodies. For instance, the toxicity of allyl sulphocyanide is much greater than that of the corresponding saturated compound. The influence of the position of the double bond upon toxicity may also be seen in the safrol series. Safrol, with its allyl-group, is considerably more poisonous than is \( \beta \)-safrol with the propenyl group in the side-chain. Chemically, the phenyl-allyl compounds react much more readily than the corresponding propenyl compounds; in the latter the double bond is conjugated with the double bond of the benzene nucleus; in the former it is not.

Among the terpenic bodies, pulegone causes fatty degeneration of the organs and phosphorism, while menthone, which is derived from the addition of hydrogen to the double bond of pulegone, is much less poisonous. Its physiological action also is less pronounced than that of carvone, which has a double bond in the side-chain.

It is also stated that the allyl ethers myristicine, apiol and 1-allyl-2,3,4,5-tetramethoxy benzene, which possess a pronounced physiological action, owe their toxicity in part to their unsaturated side-chain.

H. Fühner\(^3\) has investigated the ratio of activity of the following univalent alcohols, \( \text{viz.} \), methylalcohol, ethylalcohol, \( n \)-propylalcohol, \( n \)-butylalcohol, \( n \)-amylalcohol, \( n \)-hexylalcohol, \( n \)-heptylalcohol and \( n \)-octylalcohol upon erythrosites, sea-urchins’ eggs, convoluta and phoxinus.

**Phyto-physiological Notes.**

The *Atti R. Accad. dei Lincei, Roma* (5), 20 (1911), II. p. 349, of which Sig. I. Giglioli\(^3\) has kindly sent us a copy, contain an article from his pen on the probable function of the essential oils and other volatile con-

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\(^1\) Apotheker Ztg. 26 (1911), 785.

\(^2\) Zeitschrift für Biologie 57 (1912), 465. From a reprint kindly sent to us.

\(^3\) Quoted from Chem. Zentralbl. 1912, I. 271.
constituents of plants as the cause of the movement of the juices in the vegetable tissues. According to the author's theory the essential oil, by affecting the surface-tension of the water, causes a movement in the plant-juices containing the enzymes, or the substances in which the enzymes are capable of effecting a change. This movement produces enzymatic reactions, in the course of which certain special bodies undergo decomposition, which in turn results in an increase of osmotic pressure, causing a renewed flow of water. In fact, the accumulation of water in the tissues is frequently connected with enzymatic action, as the author has already demonstrated on previous occasions. Not only chloroform, benzene, toluene and other compounds, but also many essential oils increase the juiciness of the tissues by allowing the water to vacate the cells and by driving the plant-juice through membranes which under other conditions it is unable to penetrate. Besides water certain other readily hydrolysable compounds are split-off, simultaneously with enzymes, which possess the power of resolving complex into simple compounds. These processes again cause fresh accumulations and movements of the water. Dried, compressed yeast, when exposed to the action of chloroform, eucalyptus oil, camphor oil, or camphor becomes soft within the course of a few hours, and after a few days it is possible to filter the juice through paper or porous porcelain. This juice contains zymase and produces alcoholic fermentation in solutions of cane-sugar or glucose. Zymase is more easily obtainable by this process than by the familiar methods. The process may also be usefully applied in the study of the toxicity of fungi and other vegetable substances. Giglioli, for instance, has tested the action of 128 essential oils and other volatile bodies upon green, newly-gathered cherry-laurel leaves, and has found that in almost every instance hydrocyanic acid was liberated 1). The author surmises that all aromatic substances which are generated in plants would set up a similar movement of the juices in cherry-laurel leaves. According to Giglioli the part played by the essential oils in the organism of the conifers consists of promoting the flow of water through the cells and membranes, of acting as carriers of enzymes and soluble constituents and of causing enzymatic action by which the movement of the juices is favoured and increased.

The oil content of several different plants has been determined at Buitenzorg 2) as follows: 50 kilos green peel of Djeroek dalima yielded 2,7 cc. oil; 7,5 kilos dry buds of Gnaphalium javanicum 3) contained 3,5 cc.

1) Similar observations on the action of volatile bodies upon plants which contain odorous substances in the form of glucoside-compounds have been quoted by us on previous occasions. Comp. Report April 1910, 161; April 1911, 159.

2) Jaarb. dep. landb. in Ned.-Indië, Batavia 1910, 50.

3) Gnaphalium javanicum, Reinw. = Antennaria javonica, D. C. (according to the Index Kewensis).
of an oil with a terpene-like odour; 5.15 kilos pelargonium branches (a hybrid of Pelargonium Radula, l'Hér. and P. graveolens, l'Hér.) when distilled yielded 3 cc. oil; 5 kilos leaves of Dryobanalops aromatic, Gaertn. yielded 54 cc. oil.

On p. 41 of the present Report we refer to Brooks's discovery of the occurrence of an oxidase in the flowers of Michelia Champaca. Brooks¹) has discovered the presence of enzymes with an oxidative action not only in the above-named flowers, but in many other plants yielding volatile oils and it would appear as if these bodies were of considerable importance in the formation of certain constituents of essential oils. For example, Lecomte²) surmises that in the vanilla-plant coniferyl alcohol is converted by an oxidase into vanillin. The fact that the menthone in the peppermint herb and the carvone in the caraway plant are principally formed only during the flowering-season, points to the probability that the generation of these oxygenated bodies is connected with the presence of an oxidative enzyme. As a matter of fact, Brooks has succeeded in tracing the occurrence of oxidase in the peppermint herb and in several other plants.

In order to establish this fact, the fresh plants were ground with clean quartz sand and a little water to the consistency of a paste, from which he pressed a juice. This he tested with several reagents (guaiac resin, pyrogallol, phenolphthalein) for the presence of enzymes with an oxidative action, and thus he succeeded in demonstrating the occurrence of an oxidase in the pressed juice of green caraway fruit. In the peppermint herb the enzymes with oxidative action occur chiefly in the inflorescence; the oxidase-reactions being very feeble with non-flowering plants. In addition to Mentha piperita, the author obtained active extracts from Mentha viridis, M. crispa, M. sylvestris and M. gentilis. The peppermint herb contains a catalase as well as an oxidase. 25 g. Peppermint flowers yielded 25 cc. extract, of which 5 cc. liberated 42 cc. oxygen from 10 cc. 3% hydrogen peroxide solution within the space of 6 minutes. Valerian root contains an enzyme (lipase) which splits up fatty bodies. Brooks has also established oxidase in tansy leaves, in the leaves of Thuja occidentalis, and in the herb of Satureja montana and of Calamintha officinalis.

With roses and with palmarosa grass the test for oxidases resulted negatively, and this explains why the oils of these plants contain large proportions of alcohols and but little aldehydes.

The fact that the scent of many flowers deteriorates shortly after the gathering gives rise to the surmise that the flowers contain oxidases. Brooks is of opinion that flowers of this kind are not well suited for enfleurage.

²) Compt. rend. 133 (1901), 745; Journ. de Pharm. et Chim. 17 (1903), 341; Comp. Report October 1903, 104.
In our April Report of 1911, p. 167, we mentioned that Klobb, Garnier and Ehrwein had recovered hydrocarbons from the dried flowers of a large number of plants. Klobb\(^1\), after removing the hydrocarbons, has isolated from the ethereal or alcoholic extract of the flowers of *Matricaria Chamomilla*, *Tilia europaea*, *Linaria vulgaris* and *Verbascum Thapsus*, \(l\)-phytosterols possessing the following melting-points: 120 to \(131^\circ\), 126\(^\circ\), 133 to \(138^\circ\) and 142 to \(144^\circ\).

In our last Report (p. 124) we stated that Sack had detected the presence of indole in the flowers of various *Citrus*-species. We gather from the *Apotheker Zeitung\(^2\)* that Sack has also found the same body in the aroma of the flowers of *Citrus Medica*, L. and *C. Limetta*, Risso.


**Chemical Notes.**

With the object of discovering a standard for the unsaturated character of hydroaromatic compounds, J. Klimont and W. Neumann\(^4\) have investigated the conditions under which the absorption of bromine by unsaturated compounds takes place quantitatively. Working according to the equation

\[5K\text{Br} + K\text{BrO}_3 + 3H_2\text{SO}_4 = 3K_2\text{SO}_4 + 3H_2O + 3\text{Br}_2\]

good results were obtained. The generation of halogen oxide compounds is prevented by adding sulphuric acid. The determination is carried out by dissolving a few decigram of the terpene in chloroform, diluting the mixture with a known quantity of an aqueous solution of potassium bromide and potassium bromate in the proportions indicated by the above equation, adding sulphuric acid (1:2) and shaking. Iodide of potassium is then added in excess and the iodine liberated is titrated.

**Hydrocarbons.**

A paper by A. F. Sievers\(^5\) on the absorption of organic acids by unsaturated hydrocarbons contains some interesting data on the behaviour of these acids, particularly glacial acetic acid, towards pinene and limonene.

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\(^3\) Chem. News 104 (1911), 276. Quoted from Pharmaceutical Journ. 87 (1911), 81.

\(^4\) Pharm. Post 44 (1911), 587. Quoted from Chem. Zentralbl. 1911, II. 953.

\(^5\) Bull. of the Univers. of Wisconsin, Science Series, 4 (1911), 39 (No. 434). From a reprint kindly sent to us.
Table I.

<table>
<thead>
<tr>
<th>Mixture consisting of</th>
<th>Date</th>
<th>d&lt;sub&gt;20&lt;/sub&gt;</th>
<th>[α]&lt;sub&gt;d20&lt;/sub&gt;</th>
<th>% Ester calc. as pinene- or limonene- &quot;acetate&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 vol.&lt;sup&gt;1)&lt;/sup&gt; pinene + 1 vol. glacial acetic acid</td>
<td>27. 8. 06</td>
<td>0.9400</td>
<td>+8°31'</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1. 11. 06</td>
<td>0.9450</td>
<td>-7°50'</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>13. 12. 06</td>
<td>0.9460</td>
<td>-7°45'</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td>15. 5. 07</td>
<td>0.9502</td>
<td>+7°18'</td>
<td>7.40</td>
</tr>
<tr>
<td></td>
<td>7. 12. 09</td>
<td>0.9590</td>
<td>+3°15'</td>
<td>18.3</td>
</tr>
<tr>
<td>1 vol. pinene + 2 vols. glacial acetic acid</td>
<td>27. 8. 06</td>
<td>0.9744</td>
<td>+6°8'</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1. 11. 06</td>
<td>0.9769</td>
<td>-4°50'</td>
<td>3.03</td>
</tr>
<tr>
<td></td>
<td>13. 12. 06</td>
<td>0.9785</td>
<td>-4°35'</td>
<td>4.83</td>
</tr>
<tr>
<td></td>
<td>15. 5. 07</td>
<td>0.9804</td>
<td>+4°15'</td>
<td>9.05</td>
</tr>
<tr>
<td></td>
<td>7. 12. 09</td>
<td>0.9960</td>
<td>+2°13'</td>
<td>28.70</td>
</tr>
<tr>
<td>1 vol. limonene + 1 vol. glacial acetic acid</td>
<td>29. 11. 06</td>
<td>0.9380</td>
<td>+47°30'</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4. 1. 07</td>
<td>0.9388</td>
<td>+47°10'</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>15. 3. 07</td>
<td>0.9392</td>
<td>+47°32'</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>15. 5. 07</td>
<td>0.9400</td>
<td>+47°0'</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>7. 12. 09</td>
<td>0.9470</td>
<td>+38°39'</td>
<td>12.90</td>
</tr>
<tr>
<td>1 vol. limonene + 2 vols. glacial acetic acid</td>
<td>29. 11. 06</td>
<td>0.9733</td>
<td>+31°52'</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4. 1. 07</td>
<td>0.9737</td>
<td>+31°0'</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>15. 3. 07</td>
<td>0.9744</td>
<td>+31°25'</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>15. 5. 07</td>
<td>0.9748</td>
<td>+31°43'</td>
<td>2.74</td>
</tr>
<tr>
<td></td>
<td>7. 12. 09</td>
<td>0.9880</td>
<td>+28°42'</td>
<td>10.07</td>
</tr>
<tr>
<td>1 vol. limonene + 1 vol. glacial acetic acid + 1.11 g. HCl</td>
<td>29. 11. 06</td>
<td>0.9390</td>
<td>+47°35'</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4. 1. 07</td>
<td>0.9403</td>
<td>+47°20'</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>15. 3. 07</td>
<td>0.9402</td>
<td>+47°38'</td>
<td>2.93</td>
</tr>
<tr>
<td></td>
<td>15. 5. 07</td>
<td>0.9408</td>
<td>+46°45'</td>
<td>2.78</td>
</tr>
<tr>
<td></td>
<td>7. 12. 09</td>
<td>0.9430</td>
<td>+46°16'</td>
<td>7.47</td>
</tr>
<tr>
<td>1 vol. limonene + 2 vols. glacial acetic acid + 1.11 g. HCl</td>
<td>29. 11. 06</td>
<td>0.9742</td>
<td>+31°50'</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4. 1. 07</td>
<td>0.9750</td>
<td>+31°30'</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>15. 3. 07</td>
<td>0.9750</td>
<td>+31°20'</td>
<td>3.14</td>
</tr>
<tr>
<td></td>
<td>15. 5. 07</td>
<td>0.9754</td>
<td>+31°25'</td>
<td>3.78</td>
</tr>
<tr>
<td></td>
<td>7. 12. 09</td>
<td>0.9770</td>
<td>+30°20'</td>
<td>9.39</td>
</tr>
<tr>
<td>1 vol. limonene + 1 vol. glacial acetic acid + 2.5 g. dehydrated sodium acetate</td>
<td>29. 11. 06</td>
<td>0.9414</td>
<td>+47°40'</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4. 1. 07</td>
<td>0.9440</td>
<td>+46°25'</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>15. 3. 07</td>
<td>0.9464</td>
<td>+46°0'</td>
<td>2.88</td>
</tr>
<tr>
<td></td>
<td>15. 5. 07</td>
<td>0.9490</td>
<td>+45°15'</td>
<td>5.19</td>
</tr>
<tr>
<td></td>
<td>7. 12. 09</td>
<td>0.9710</td>
<td>+35°45'</td>
<td>33.30</td>
</tr>
<tr>
<td>1 vol. limonene + 2 vols. glacial acetic acid + 2.5 g. dehydrated sodium acetate</td>
<td>29. 11. 06</td>
<td>0.9758</td>
<td>+31°50'</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4. 1. 07</td>
<td>0.9758</td>
<td>+31°4'</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>15. 3. 07</td>
<td>0.9785</td>
<td>+31°0'</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td>15. 5. 07</td>
<td>0.9798</td>
<td>+31°12'</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td>7. 12. 09</td>
<td>0.9870</td>
<td>+28°58'</td>
<td>15.95</td>
</tr>
</tbody>
</table>

<sup>1)</sup> 500 cc.
Table II. Heating in pressure-bottles.

<table>
<thead>
<tr>
<th>Mixture consisting of</th>
<th>Period of Heating</th>
<th>$d_{20}$</th>
<th>$[\alpha]_{D20}$</th>
<th>$%$ Ester</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 vol. pinene + 1 vol. glacial acetic acid . .</td>
<td>8 hours 24 &quot;</td>
<td>0.9465</td>
<td>$+ 4^\circ 25'$</td>
<td>5,80</td>
<td>100$^\circ$</td>
</tr>
<tr>
<td>1 vol. pinene + 2 vol. glacial acetic acid . .</td>
<td>8 hours 24 &quot;</td>
<td>0.9807</td>
<td>$+ 2^\circ 33'$</td>
<td>8,58</td>
<td>100$^\circ$</td>
</tr>
<tr>
<td>1 vol. pinene + 1 vol. glacial acetic acid . .</td>
<td>8 hours 24 &quot;</td>
<td>0.9590</td>
<td>$+ 4^\circ 40'$</td>
<td>13,12</td>
<td>100$^\circ$</td>
</tr>
<tr>
<td>1 vol. pinene + 2 vol. glacial acetic acid . .</td>
<td>8 hours 24 &quot;</td>
<td>0.9962</td>
<td>$+ 2^\circ 35'$</td>
<td>25,50</td>
<td>140–150$^\circ$</td>
</tr>
<tr>
<td>1 vol. pinene + 1 vol. glacial acetic acid . .</td>
<td>8 hours 24 &quot;</td>
<td>0.9517</td>
<td>$+ 3^\circ 0'$</td>
<td>25,40</td>
<td>140–150$^\circ$</td>
</tr>
<tr>
<td>1 vol. pinene + 2 vol. glacial acetic acid . .</td>
<td>8 hours 24 &quot;</td>
<td>0.9895</td>
<td>$+ 2^\circ 37'$</td>
<td>25,3</td>
<td>175–185$^\circ$</td>
</tr>
</tbody>
</table>

Sievers prepared a set of mixtures of pinene with equal and with double quantities by volume of glacial acetic acid, and a corresponding set of limonene mixtures. In some of the latter he introduced into the solution a known weight of hydrogen chloride. Finally, Sievers made experiments with limonene with an equal and a double volume of glacial acetic acid with the addition of a known weight of sodium acetate. The density, rotation, and ester value of these mixtures were repeatedly determined within a period of from 7 to 9 months, and again after 2 $\frac{1}{2}$ years. Part of the figures ascertained by Sievers are reproduced in table (I) (p. 166) below.

The figures in the above table show that by adding sodium acetate pinene and limonene are more ready to combine with acetic acid than is the case when adding hydrochloric acid.

The pinene was heated with glacial acetic acid in pressure-bottles at high temperatures and the ester of these mixtures was determined.
According to Sievers the reactions which take place at room-temperature are due to simple absorption, whereas at high temperatures the acid unquestionably attacks the molecule. The same experiments were repeated at atmospheric pressure by heating in a reflux condenser. In both cases the ester value was found to be much higher than in the previous experiments. A few of the values determined by Sievers are given in the table (II) (p. 167) below.

The findings of Sievers described above made it appear desirable to determine the extent to which acetic anhydride reacts with pinene and limonene under experimental conditions similar to those observed in acetylating essential oils. Several samples of freshly purified and rectified terpenes, when treated in this manner, gave an ester value after acetylation of not more than \(1,8 = 0,5\% \text{C}_{10}\text{H}_{15}\text{O}\), a value which is negligible in practice, and is therefore without effect in the alcohol-determination of essential oils. The values are slightly higher with impure hydrocarbons, or hydrocarbons which are somewhat resinified as a result of prolonged keeping. Where such was the case we observed an ester value after acetylation ranging, according to the age of the sample, up to \(15 = 4,2\% \text{C}_{10}\text{H}_{15}\text{O}\); a pinene which was more than four years old registering as much as \(38,2 = 10,8\% \text{C}_{10}\text{H}_{15}\text{O}\).

Camphene. K. Auwers\(^1\) in a paper on the constitution of camphene, refers to the recent work of Aschan and Lipp\(^2\) on this hydrocarbon. The progress attained by the researches embodied in that work lies in the proof which has been afforded that, contrary to the opinions of Moycho and Zienkowsky, the camphenes of different origin are in their essentials of a uniform character and represent one and the same hydrocarbon. In the present state of our knowledge however it appears to be impossible to draw positive conclusions with regard to the constitution of the hydrocarbon from the chemical conversions of camphene alone. But in the case under review it would appear that the spectrochemical behaviour scarcely leaves room for doubt as to the group of hydroaromatic compounds to which the hydrocarbon belongs. To obtain useful results it is necessary, when calculating the spectrochemical data, to compare the latter with water at 4°. In comparing the statements of Wallach, Brühl, Eijkman, and Helle on the refraction and density of camphene, it will be found that they have all been estimated at temperatures ranging from 40 to 78°, but the estimated values may be converted with sufficient accuracy to 50°. Having done this, Auwers ascertained the mean of the camphene-values found by the above-mentioned authors to be \(M_\alpha 43,73\) and

\(^1\) Liebigs Annalen 887 (1912), 240.
\(^2\) Comp. Report April 1911, 188; October 1911, 132, 135.
These results show that it is practically certain that camphene cannot be a saturated body with a tricyclic ring, because the excess of the ascertained mean values of refraction over the values calculated for the saturated formula \( \text{C}_{10}\text{H}_{16} \) is not less than +2.12 and +2.14. It is true that a tricyclic ring also effects a rise in refraction but not by far to such an extent as indicated in these excess-values. From the observations on cyclene, \( \beta \)-bornylene and \( \beta \)-pinolene, all of which are saturated tricyclic compounds, it is clear that in a tricyclical system the tricyclic ring claims a similar, and apparently only slightly larger increment than in other cyclical bodies. From the spectrochemical observations which have been made within the past few years it may be stated with certainty that camphene cannot be a saturated compound. The examination of seven different camphene-preparations has shown the molecular refraction of camphene to be larger than that calculated for the formula \( \text{C}_{10}\text{H}_{16} \), and the exaltations to equal \( E\Sigma_a = +0.32 \) and \( E\Sigma_D = +0.37 \). This behaviour points to the semicyclic structure of camphene, and would appear to afford spectrochemical proof of the corrections of Wagner's camphene formula.

What has been stated above with regard to camphene is also applicable to \( D-l \)-fenchene and to its optical antipode, \( L-d \)-fenchene. Here, \( E\Sigma_D = +0.33 \), a fact which can only be explained on the hypothesis of a semi-cyclic double linking. Accordingly, the formula of \( D-l \)-fenchene would be that given by Wallach and almost universally accepted.

G. G. Henderson and Miss M. M. J. Sutherland\(^1\) have described as camphylic acid an acid which they had obtained from camphene by oxidising it with hydrogen peroxide. In a supplementary notice they state\(^2\) that Bredt has called their attention to the fact that Perkin had also applied the name of camphylic acid to the acid obtained by him by fusing sulphocamphylic acid with alkalis. Moreover, Aschan informed them that an acid apparently identical with camphylic acid had been obtained by him by oxidising camphene with potassium permanganate at a low temperature in acetic acid solution, and that he has suggested the name

\(^1\) Comp. Report October 1911, 134.
\(^2\) Proceed. chem. Soc. 27 (1911), 279.
of "camphenanic acid" for this body. As a result of these communications Henderson and Miss Sutherland announce that they will in future call their camphylic acid "camphenanic acid".

**Bornylene.** As stated on p. 171, the conversion of bornylene into camphenilanaldehyde points to the close relationship of the camphene and bornylene nuclei. According to G. G. Henderson and I. M. Heilbron\(^1\) the conversion may be represented by the formulæ given below, it being assumed that an oxide-like body is formed as an intermediary product. On the basis of this conversion, as well of theoretical considerations which we have not space to repeat here, the authors regard Semmler's old camphene-formula as the most likely to be correct.

\[
\begin{align*}
\text{Bornylene.} & \quad \text{Oxide-like intermediary product.} \\
\hline
\text{Camphenilanolic aldehyde.} & \quad \text{Semmler's old camphene formula.}
\end{align*}
\]

G. G. Henderson\(^3\), who, with various collaborators, had previously investigated the action of chromyl chloride upon limonene, pinene, and terpinene, has recently, together with I. M. Heilbron\(^3\), oxidised bornylene with chromyl chloride and has also studied the behaviour of the hydrocarbon when attacked by nitric and nitrous acids. Reaction of chromyl chloride with bornylene which had been dissolved in carbon disulphide gave rise in the first place to an additive product \(\text{C}_{10}\text{H}_{16}, 2\text{Cr}_2\text{O}_2\text{Cl}_2\), which upon the addition of ice was converted into a chloroketone \(\text{C}_{10}\text{H}_{15}\text{OCl}\)

---

\(^1\) Journ. chem. Soc. 99 (1911), 1901.

\(^2\) Comp. Report April 1908, 180; November 1908, 171; October 1909, 176.

\(^3\) Journ. chem. Soc. 99 (1911), 1887.
and an aldehyde $\text{C}_9\text{H}_{16}\text{CHO}$. The chloroketone proved to be a hitherto unknown chlorocamphor, of which the semicarbazone melted at 234 to 235°, and yielded camphoric acid when oxidised with permanganate of potassium, and camphor when heated with alcoholic potash liquor in a sealed tube at 150 to 160°. The aldehyde $\text{C}_9\text{H}_{16}\text{CHO}$ could be purified from the primarily produced bisulphite-compound, and was identified as camphenilanic aldehyde. This aldehyde being a true camphene derivative, its generation from bornylene points to the relationship of this hydrocarbon with camphene. When exposed to air, camphenilanaldehyde was oxidised to a mixture of camphenilanic acid (m. p. 65°) and isocamphenilanic acid (m. p. 118°). Camphenilanic acid is very readily converted into the iso-modification, repeated recrystallisation from water, alcohol or light petroleum being sufficient to effect the conversion. When semicarbazide is allowed to act upon camphenilanaldehyde, isocamphenilanaldehyde semicarbazone (m. p. 191 to 192°) is formed. Bromoisocamphenilanic acid (m. p. 204 to 205°) was prepared by the authors by heating isocamphenilanic chloride with bromine under pressure, and decomposing the brominated chloride with water. Heating bromoisocamphenilanic acid with aqueous soda solution gave rise to an unsaturated acid $\text{C}_9\text{H}_{13}\cdot \text{CO}_2\text{H}$ (m. p. 147°).

Henderson and Heilbron also acted with nitrous acid upon bornylene, by overlaying concentrated aqueous sodium nitrite solution with a solution of bornylene in light petroleum, and gradually adding glacial acetic acid. They obtained the following reaction-products: 1. Bornylene nitrosite (C$_{10}$H$_{15}$N$_2$O$_3$)$_2$, m. p. 163°, which was oxidised into camphoric acid. 2. An oily liquid, perhaps bornylene isonitrosite. 3. Camphorquinone (m. p. 197 to 198°) and 4. a crystalline body, m. p. 84 to 85°, perhaps a bornylene nitrite. With nitric acid, bornylene was oxidised into a mixture of camphoric acid and a body $\text{C}_{10}\text{H}_{16}\text{O}_4\text{N}_3$, crystallising in yellow needles, which was identified as to be a dinitrocamphane.

The bornylene employed for these reactions was prepared by Tschugaeff's method from borneol from primarily-produced bornyl methylxanthogenate-

On the constitution of $D$-l-fenchene see p. 169.

$\alpha$-Pinene. Mario Mayer$^1$) has published an historical résumé of the researches into pinene, and of the relations of pinene to camphor and to other bodies of similar chemical structure. From its nature it follows that the publication is chiefly retrospective and that the new experimental material contained in it is of subordinate interest, the principal reference of this character being that dealing with the splitting-up of the hydroxylamine oxime of $l$-$\alpha$-pinene by means of $\alpha$-bromo-$\tau$-camphor sulpho-acid.

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$^1$) *Tesi di libera docenza, R. Instituto di Studi sup.*, Florence 1911. Our best thanks are due to the author for kindly sending us a copy of the pamphlet.
The author has succeeded in converting the inactive hydroxylamine oxime (decomposition-point 140°), into two salts of the acid in question (decomposition-points 195 and 172° respectively). When the salts were resolved with soda they gave rise respectively to a dextrorotatory and a laevorotatory oxime, decomp. pts. 147 and 145°, \([\alpha]_D\) in methylalcoholic solution + 60,74 and — 59,66°.

Iso-pinene. N. Zelinsky\(^1\) describes isopinene, a hydrocarbon which is an isomeride of \(\alpha\)-pinene. With the object of preparing this body, 1-\(\alpha\)-pinene (b. p. 155 to 155,5°; \(d_{40}^{20} 0,8587\); \([\alpha]_D\) — 43,81°; \(n_{D20} 1,4652\) in absolute ethereal solution was allowed to react with palladium black. After a few hours, hydrogen was passed into the liquid at ordinary temperature, giving rise to isopinene possessing the following constants: b. p. 158,5 to 159,5°, \(d_{40}^{20} 0,8573\), \([\alpha]_D\) — 38,09°, \(n_{D20} 1,4641\). Neither hydrochloride nor nitrosochloride is formed. Zelinsky assumes that \(\alpha\)-pinene first absorbs hydrogen, under formation of hydropinene, and that isopinene results from the latter, somewhat after the following reaction:

\[
\begin{align*}
\text{CH} & + \text{Pd} + \text{H}_2 \rightarrow \\
\text{CH} & + \text{Pd} \rightarrow \\
\text{CH} & + \text{H}_2 + \text{Pd}
\end{align*}
\]

The behaviour of \(\alpha\)-pinene towards palladium black is very different when it is exposed for a period of 4 weeks to the action of hydrogen under very low pressure. In this case it yields hydropinene (b. p. 167,5 to 168°; \(d_{40}^{20} 0,8567\); \([\alpha]_D\) — 19,84°; \(n_{D20} 1,4605\)). When reducing \(\alpha\)-pinene by Sabatier's method, the author obtained a mixture of two hydrocarbons (b. p. 163,5 to 165° and 168 to 168,5°).

Iso-pinene, the hydrocarbon which was described by Aschan\(^2\) a few years ago, is not identical with Zelinsky's isopinene, as is evident from a comparison of the constants, as well as from the structural formulæ given by the respective authors. Apparently Zelinsky has overlooked Aschan's publication, otherwise he would certainly have named his hydrocarbon differently.

\(^1\) Berl. Berichte 44 (1911), 2782.

Menthadiene. Some years ago we reported that Brunel\textsuperscript{1} has obtained a menthene by heating thymomenthol with bisulphate of potassium or phosphorus pentoxide. In view of the fact that the process of eliminating water by the aid of these reagents tends to bring about intramolecular rearrangements, G. G. Henderson and R. Boyd\textsuperscript{2} have synthetised this menthene by heating thymomenthol with an aqueous solution of oxalic acid, thereby obviating the risk of intramolecular rearrangements. The $\Delta^2$-menthene prepared by this method had the same properties as Brunel's thymomenthene: b. p. 167 to 169\textdegree, $d_{20}^{20}$ 0.8188, $n_D$ 1.45363. It yields a nitroso chloride, m. p. 133\textdegree. With bromine a dibromide is formed, from which, when boiled with an excess of alcoholic potash liquor, a menthadiene (m. p. 173.5; $d_{20}^{20}$ 0.8337; $n_D$ 1.46539) results. This is probably a $\Delta^{2,4}$-menthadiene. As it was interesting to compare the terpenes with isomeric hydrocarbons $C_{10}H_{18}$, Henderson and Boyd prepared 1,3-diethylcyclohexadiene from phenol, by converting phenol into 3,5-diethylphenol, and reducing the latter to 1,3-diethylcyclohexanol. Boiling diethylcyclohexanol with oxalic acid solution gave rise to a mixture consisting for the greater part of 1,3-diethylcyclohexene, contaminated with diethylcyclohexadiene. This mixture was converted into diethylcyclohexene dibromide, from which, when boiled with an excess of alcoholic potash liquor 1,3-diethylcyclohexadiene (b. p. 166 to 168\textdegree; $d_{20}^{20}$ 0.8659; $n_D$ 1.47575) resulted. The double bond is probably in the 3,5-position.

Cedrene. A few years ago Semmler and Hoffmann\textsuperscript{3}, while oxidising cedrene with permanganate of potassium in acetone solution, obtained a keto aldehyde or a diketone, together with a cedrene keto acid. In order to gain further insight into the molecular structure of cedrene, Semmler and F. Risse\textsuperscript{4}, have now subjected fairly large quantities of cedrene to oxidation with ozone in glacial acetic acid, as a result of which they obtained oxidation products which in many respects were similar to those prepared with permanganate of potassium. The cedrene employed in the oxidation process boiled between 123 and 124\textdegree (12 mm.). The neutral oxidation products formed consisted of a ketone $C_{14}H_{24}O$ or $C_{14}H_{22}O$ (m. p. of the semicarbazone 218\textdegree), and a keto aldehyde $C_{15}H_{24}O_2$. If the ketone possessed the formula $C_{14}H_{22}O$, it would follow that, in addition to the cedrene which was not saturated in the ring (from which only a ketone $C_{14}H_{24}O$ could originate), a semicyclic cedrene was admixed to the natural cedrene.

As an acid oxidation product an acid $C_{15}H_{24}O_9$, cedrene keto acid was isolated. The methyl ester of this acid possessed the following con-

\textsuperscript{1} Comp. Report April 1905, 103.
\textsuperscript{2} Journ. chem. Soc. 99 (1911), 2159.
\textsuperscript{3} Comp. Report April 1908, 28.
\textsuperscript{4} Berl. Berichte 45 (1912), 355.
When oxidised with 27% nitric acid, cedrene keto acid yields an acid \( \text{C}_9\text{H}_{12}\text{O} \) (m. p. 182.5°), to which the authors give the name of cedrene dicarboxylic acid, and of which the dimethylester had the following characters: b. p. 179 to 183° (13 mm.), d\( \text{D} \) 1.0778, \( \alpha_\text{D} \) = 31°36', n\( \text{D} \) 1.48084.

The fact that cedrene keto acid \( \text{C}_{15}\text{H}_{24}\text{O}_3 \) is a methyl keto acid, which compares uniformly with dicarboxylic acid \( \text{C}_{14}\text{H}_{22}\text{O}_4 \) was confirmed by its giving rise to dicarboxylic acid when oxidised with alkaline bromine solution.

Semmler and Risse consider that the preparation of cedrene dicarboxylic acid \( \text{C}_{14}\text{H}_{22}\text{O}_4 \) affords an excellent means of detecting the presence of cedrene in essential oils.

\text{Caryophyllene.} So far, the santalols and santalenes were the only sesquiterpene bodies of which the structure was known, but recently Semmler and E. W. Mayer\(^1\) have succeeded in clearing up the principal outlines of the molecular structure of caryophyllene. As the researches of Deussen\(^2\) have shown caryophyllene to consist of a mixture of several hydrocarbons, it was not an easy matter to elucidate the structure of this body. The proneness of caryophyllene to inversion renders its investigation extraordinarily difficult. For example, the authors look upon the compound \( \text{C}_{14}\text{H}_{22}\text{O} \), which was obtained by Deussen and by Haarmann\(^3\) in the course of oxidation with permanganate of potassium, as being not a derivative of the original caryophyllene, but a product of inversion, possibly of tricyclic \textit{iso}caryophyllene. The only method by which useful results can be expected is oxidation with ozone, and as a matter of fact, Semmler and Mayer have succeeded, by gradually oxidising caryophyllene by means of ozone, in obtaining bodies which are in the main derived from two caryophyllenes. These they call \textit{terp.-caryophyllene} and \textit{lim.-caryophyllene}, and they assign to them for the present two formulæ which are analogous to those of terpinolene and limonene, as follows:

\[
\begin{align*}
\text{Terp.-Caryophyllene.} & \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
& \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
& \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
& \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
& \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
\text{Lim.-Caryophyllene.} & \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
& \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
& \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
& \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
& \quad \text{H}_2\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H}_2 \\
\end{align*}
\]

\(^1\) Berl. Berichte 44 (1911), 3657.
\(^2\) Comp. Report November 1908, 176; April 1909, 124; October 1909, 177; April 1910, 169.
\(^3\) Comp. Report October 1909, 177.
In the course of the ozonising process acid and neutral decomposition products were obtained. Among the former was a ketocarboxylic acid, \( \text{C}_{11}\text{H}_{18}\text{O}_8 \) (b. p. 183 to 187° at 11,5 mm.; m. p. of the semicarbazone 183°), and a diketocarboxylic acid \( \text{C}_{14}\text{H}_{22}\text{O}_4 \) (b. p. 229 to 232° at 11,5 mm.). The neutral decomposition products consisted of a ketone \( \text{C}_{10}\text{H}_{15}\text{O} \) (b. p 73 to 76° at 11,5 mm.; m. p. of the semicarbazone 176°), a diketone \( \text{C}_{12}\text{H}_{20}\text{O}_2 \) (b. p. 137 to 142° at 9 mm.; m. p. of the semicarbazone 219°) and a diketonic acid \( \text{C}_{9}\text{H}_{14}\text{O}_4 \), b. p. 222 to 225° (13 mm.) to which the authors give the name of caryophyllenic acid. This body could not be obtained in the crystalline form, and the attempts made by us, at Semmler's suggestion, to crystallise the acid by strong cooling remained without result. Caryophyllenic acid closely resembles pinic acid, but, unlike the latter, it yields an anhydride (b. p. 152 to 158° at 10 mm.). The dimethyl ester of caryophyllenic acid gives the following constants: b. p. 127 to 131° (11 mm.), \( d_{20}^0 \) 1,0456, \( \alpha_{20}^0 + 44^\circ \), \( n_{D20}^0 \) 1,4462. In addition to caryophyllenic acid the oxidation of the acid \( \text{C}_{11}\text{H}_{18}\text{O}_3 \) had yielded dimethyl succinic acid. The identical products of oxidation are obtained when the keto acid is treated with bromine solution. Semmler and Mayer conceive the generation of ketocarboxylic acid from the ozonide to proceed as follows:

\[
\text{Terp.-Caryophyllene} + \text{Ozone} \rightarrow \text{Caryophyllenic acid.}
\]

\[
\text{Ketocarboxylic acid.}\n\]

\[
\text{Caryophyllenic acid.}\n\]

\[
\text{Dimethylsuccinic acid.}\n\]

The diketocarboxylic acid \( \text{C}_{14}\text{H}_{22}\text{O}_4 \) was further oxidised with nitric acid, when it yielded an oil studded with crystals which proved to consist
of succinic acid (m. p. 182°). When fractionated the oil yielded succinic anhydride as well as caryophyllenic acid.

The authors conceive the diketo acid to be a derivative of lim.-caryophyllene, possibly according to the following reaction:

\[
\text{Lim.-Caryophyllene} + \text{Ozone} \rightarrow \text{Diketo acid, or Diketo aldehyde.}
\]

\[
\text{Caryophyllenic acid} + \text{HOOC} \rightarrow \text{Succinic acid.}
\]

In the course of the distillation of the acid oxidation products the first runnings consisted of an acid \( \text{C}_8\text{H}_{14}\text{O}_2 \), b. p. 120 to 128° (9 mm.), of which the amide had m. p. 96°.

The ketone \( \text{C}_{10}\text{H}_{18}\text{O} \) referred to above, when oxidised with bromine solution, yielded an acid \( \text{C}_9\text{H}_{16}\text{O}_2 \) (b. p. 131 to 133° at 13,5 mm.; m. p. of the amide 114°). Oxidation with nitric acid resulted in an acid \( \text{C}_8\text{H}_{14}\text{O}_2 \) (b. p. 119 to 122° at 12 mm.; m. p. of the amide 115 to 116°). The authors regard the ketone \( \text{C}_{10}\text{H}_{18}\text{O} \) as a secondary decomposition product of the ozonisation, and as having the following genesis:

\[
\text{Terp.-Caryophyllene} \xrightarrow{\text{HNO}_3} \text{Ketone} \xrightarrow{\text{NaOH} + \text{Br}} \text{Acid} \xrightarrow{} \text{Acid}\]
When the diketone $C_{12}H_{20}O_2$ was oxidised with nitric acid or with an alkaline bromine solution it yielded dimethyl succinic acid and caryophyllenic acid. When oxidised with permanganate of potassium the diketo aldehyde was converted into the diketo acid $C_{14}H_{22}O_4$ mentioned above. Oxidation with nitric acid, as was to be expected, yielded caryophyllenic acid and succinic acid.

It follows from the investigations summarised above that the active caryophyllenes are not, as was thought by Deussens, derivatives of naphthalene, but of the terpenes or of systems allied to the latter.

In conclusion the authors report that they have converted caryophyllene prepared according to Deussens's method into its dihydrochloride (m. p. 68 to 69°), and that this product proved to be identical with the dihydrochloride from natural caryophyllene.

Reduction of the blue caryophyllene nitrosite with sodium and alcohol afforded a body $C_{18}H_{27}N$ (b. p. 148 to 150° at 13 mm.), which is probably an amine.

On the formation of hydrocarbons from hydrazine compounds, see p. 195.

**Alcohols.**

**Dihydrolinalool.** In our last Report (p. 131) we described the alcohol dihydrolinalool, which was formed in hydrating dihydromyrcene. For purposes of comparison we had also prepared the alcohol synthetically from methylheptenone and magnesium ethyl iodide. The methylheptenone had been obtained both from citral (by oxidation), and from lemongrass oil (by treatment with bisulphite-solution). In view of the fact that, contrary to the experience with the product prepared from dihydromyrcene, we had obtained no phenylurethane with sharp m. p. from this dihydrolinalool, we also treated with magnesium ethyl iodide a methylheptenone which had been prepared by boiling citral with aqueous solution of carbonate of potassium according to Verley¹). But the dihydrolinalool prepared by this method likewise failed to yield a phenylurethane with a sharp m. p. Its constants, together with those of the products referred to above, are given in the subjoined table:

<table>
<thead>
<tr>
<th>Dihydrolinalool from</th>
<th>B. p.</th>
<th>$d_{150}$</th>
<th>$n_{D150}$</th>
<th>Mol. Found</th>
<th>Refr. Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dihydromyrcene</td>
<td>92 to 92,5° (12 to 13 mm.)</td>
<td>0,8570</td>
<td>1,45531</td>
<td>49,47</td>
<td>49,438</td>
</tr>
<tr>
<td>Methylheptenone from citral (by oxidation)</td>
<td>77 to 78° (7 mm.)</td>
<td>0,8588</td>
<td>1,45641</td>
<td>49,46</td>
<td>49,438</td>
</tr>
<tr>
<td>Methylheptenone from lemongrass oil</td>
<td>66 to 66,5° (4 mm.)</td>
<td>0,8575</td>
<td>1,45661</td>
<td>49,558</td>
<td>49,438</td>
</tr>
<tr>
<td>Methylheptenone from citral (by boiling with solution of carbonate of potassium)</td>
<td>67,5° (4 mm.)</td>
<td>0,8590</td>
<td>1,45611</td>
<td>49,424</td>
<td>49,438</td>
</tr>
</tbody>
</table>

¹) Bull. Soc. chim. III. 7 (1897), 175.
Nerol. Zeitsche ¹) has previously advanced the view that nerol is a stereoisomeride and not a structural isomeride of geraniol. Definite proof of the correctness of this theory has now been supplied by Blumann and Zeitschel²) by the oxidative resolution of nerol by Tiemann and Semmler's method. In the course of this process acetone and ëæuvlic acid were formed from nerol in the same quantitative proportions as from geraniol. The nerol used in the experiment had been prepared from oil of Helichrysum angustifolium and possessed the following constants: b. p. 225 to 226°, d₁₅₀ 0.8815, α₆₅ + 0°, m. p. of the diphenylurethane 52 to 53°. The alcohol had first been oxidised with potassium permanganate solution and afterwards with chromic acid and sulphuric acid.

\[
\text{CH}_3\text{CH} = \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH} = \text{CH}_2 \text{OH} \quad \text{Oxidation} \quad \text{CH}_3\text{CH} = \text{OH}
\]

Nerol or Geraniol.

\[
\text{CH}_3\text{CO} + \text{HO} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} + \text{HO} \cdot \text{CO} \cdot \text{CO} \cdot \text{OH}
\]

Acetone. Læuvlic acid. Oxalic acid.

Menthol. Several years ago Brunel³) showed that thymol was capable of being reduced to hexahydrothymol by Sabatier and Senderens' method. The complicated mixture which results from this conversion has been examined by R. H. Pickard and W. O. Littlebury⁴), who have isolated from it several isomeric menthols and menthones, as well as 1-methyl-3-cyclohexanol. The thymol which had remained unchanged in the reduction-process was removed from the reaction-product by treating with soda-liquor. After heating the mixture with phthalic anhydride in order to separate the alcohols, the ketones were isolated by means of semicarbazide. By repeated recrystallisation from 95% acetic acid the authors succeeded in separating two acid phthalates (m. p. 175 to 177° and 129 to 131° respectively), from the acids of the phthalic ester. The separation of the two esters is much facilitated when the dilute aqueous solution of the sodium salts is treated with magnesium chloride. The magnesium salt of the one ester is thereby precipitated in the form of a sparingly soluble compound which, after being recrystallised from alcohol, melts between 119 and 122°. When resolved with hydrochloric acid it yields the acid phthalic ester with m. p. 129 to 131°. When chloride of zinc is added to the filtrate of the magnesium salt, the zinc salt of the ester, m. p. 175

²) Berl. Berichte 44 (1911), 2591.
³) Compt. rend. 140 (1905), 252; Report April 1905, 103.
to 177° is precipitated. The filtrate of the zinc salt, upon the addition of hydrochloric acid, yielded an acid phthalate, m. p. 93°, which may also be readily separated in the form of a calcium salt. The corresponding alcohol is 1-methyl-3-cyclohexanol: b. p. 173° (752 mm.), $d^{15}_{10}$ 0.912, m. p. of the phenylurethane 96°. The phthalate with m. p. 129 to 131° is that of the $i$-menthol with m. p. 34° (b. p. 103 to 105° at 16 mm.), which yields a phenylurethane, m. p. 104° and an acid succinate, m. p. 85 to 86°. To the alcohol corresponding to the acid phthalate with m. p. 175 to 177° the authors have given the name of neo-menthol. This body melts at 51° and yields a phenylurethane with m. p. 114° and an acid succinate with m. p. 67 to 68°. $i$-Neomenthol is identical with the menthol (isomenthol) which has been obtained by Beckmann¹ by hydrolysing $l$-menthylphenylurethane with sodium ethylate at 150°. The acid menthyl phthalate, m. p. 177° and the phthalic ester which has been prepared by Enklaar² from the alcohol which had been formed by the reduction of geraniol, are also probably identical with $i$-neo-menthol. The menthol with m. p. 34° appears to be identical with Brunel's $\beta$-thymomenthol (loc. cit.) and with the menthol obtained by Kremers³ in the reduction of a synthetical menthone.

The experiments with natural $l$-menthol made by Pickard and Littlebury have demonstrated the uniformity of this alcohol. From the brucine salt of the $l$-menthyl hydrogen phthalate they recovered $l$-menthol having a specific rotation of $-49,44°$. The $i$-menthol with m. p. 34° was split up, from the primarily produced brucine salt and the cinchonine salt of the acid phthalate into $l$-menthol ($\alpha^l_{d} - 48,27°$; m. p. 42°) and $d$-menthol ($\alpha^d_{d} + 48,15°$; m. p. 40°). When splitting up $i$-neo-menthol into its optical components the authors obtained $d$-neo-menthol (b. p. 96° at 16 mm.; $\alpha^d_{d} + 19,69°$) and $l$-neo-menthol (b. p. 105° at 21 mm.; $d^{10}_{45}$ 0.8995; $\alpha^d_{d} - 19,62°; n_{D} = 1,46031$). Neither $d$- nor $l$-neo-menthol was obtained in the solid state.

When oxidised with Beckmann's chromic acid mixture, $i$-menthol yielded $i$-menthone, b. p. 205° (748 mm.) which gave rise to an oxime, (m. p. 80°) and a semicarbazone (m. p. 158°). The oxidation of $i$-neo-menthol resulted in the same $i$-menthone. From $l$-menthol the authors obtained an $l$-menthene of somewhat higher rotatory power ($\alpha^l_{d} - 29,10°$) than is stated in the literature on the subject ($\alpha^i_{d} - 24,78$ to 28,18°). The oxidation of almost pure $d$-neo-menthol led to the formation of an $l$-menthene (b. p. 204° at 750 mm.; $\alpha^d_{d} + 23,3°$); $l$-neo-menthol gave rise to $d$-menthene (b. p. 204° at 750 mm.; $\alpha^d_{d} + 24,85°$). Both $d$-menthene and $i$-neo-menthol, therefore, yield $d$-menthene, while $l$-menthol and $d$-neo-menthol both yield $l$-menthene. An analogous result takes place in the case of $l$-borneol and $d$-isoborneol, which, when oxidised, give rise to $l$-camphor.

¹) Jour. f. prakt. Chem. II. 55 (1897), 30.
²) Berl. Berichte 41 (1908), 2086.
³) Amer. chem. Journ. 18 (1896), 762.
Most interesting are the observations of Pickard and Littlebury on the occurrence of neomenthol in Japanese peppermint oil. At their request we had placed at their disposal a Japanese peppermint oil which had been freed from menthol as far as possible and which, after removal of the first and the last runnings, had been warmed with an equal quantity of benzoyl chloride. When the reaction was completed, and the hydrochloric acid had been removed by shaking with soda solution, menthone and other volatile substances were distilled off with steam. The residual esters, when saponified, yielded a mixture of alcohols from which a fraction was obtained possessing the following characters: b. p. 80 to 82° (4 mm.), $d_{150} = 0.9032$, $\alpha_D = -8^\circ 48'$ (menthol-content about 90°/o).

The authors converted this menthol fraction into its acid phthalate, which gave m. p. 140 to 143°, $[\alpha]_D = +4.5^\circ$. The ester was recrystallised 28 times from 95°/o acetic acid, after which it melted between 141 and 144°, the specific rotation being $+57.16^\circ$ (in chloroform). Mixed with $d$-neomenthyl phthalic ester, the ester melted between 142 and 144°. The alcohol which was regenerated from the ester, when oxidised with Beckmann's chromic acid mixture, yielded $l$-menthone ($[\alpha]_D = -28.33^\circ$).

The odour of $d$- and $l$-neomenthol differs altogether from that of $d$- and $l$-menthol.

The following arrangement explains the reactions described by the authors:

\[
\begin{array}{ccc}
\text{Thymol} & & \\
\text{Menthone} & & \text{Isomenthone} \\
\text{(Semicarbazone m. p. 158°)} & & \text{(Semicarbazone m. p. 217°)} \\
\text{Menthol m. p. 34°} & & \text{Neomenthol m. p. 51°} \\
\text{(Phthalic ester m. p. 130°)} & & \text{(Phthalic ester m. p. 177°)} \\
\text{$l$-Menthol} & & \text{$d$-Menthol} \\
\text{(m. p. 43° $[\alpha]_D = -49^\circ$)} & & \text{(m. p. 43° $[\alpha]_D = +49^\circ$)} \\
\text{Oxidation} & & \\
\text{$l$-Menthone} & & \text{$d$-Menthone} \\
\text{Liquid} & & \text{Liquid} \\
\end{array}
\]
P. F. Frankland and H. H. Sullivan\(^1\), when reacting with ammonia upon menthyl chloroacetate, obtained the menthyl ester of Heintz' nitrilotriacetic acid\(^2\) \(N(CH_2\cdot CO_2\cdot C_{10}H_{16})_3\), a compound which crystallises in prismatic needles; m. p. 80,5°.

**Fatty-aromatic alcohols.** At the present time we possess three methods\(^3\) for the preparation of a fatty-aromatic alcohol \(X\cdot CH_2\cdot OH\), or its halogen ester \(X\cdot CH_2\cdot Cl\) from the alcohol \(X\cdot OH\) or halogenide \(X\cdot Cl\). They are: first, condensation with cyanide of potassium, saponification of the nitrile \(X\cdot CN\) into acid, esterification into the ester \(X\cdot CO_2C_2H_5\) and reduction of this ester into the alcohol \(X\cdot CH_2OH\) according to Bouveault. Secondly, reaction with magnesium into \(X\cdot MgCl\) and conversion into the alcohol \(X\cdot CH_2\cdot OH\) by means of trihydroxymethylene according to Grignard. Thirdly, reduction of the nitrile \(X\cdot CN\) into the base \(X\cdot CH_2\cdot NH_2\) and conversion of the benzoyl-compound of the latter with phosphorus pentachloride into the chloride \(X\cdot CH_2\cdot Cl\) according to v. Braun. All three of these reactions (as v. Braun has discovered), are applicable to the halogen hydrogen esters of the phenylpropyl alcohol, but Grignard's method is the shortest and gives the highest yield of phenylbutyl alcohol. In the higher series the conditions undergo a change, inasmuch as the synthetic action of the magnesium is increased and the alcohol-yield reduced. Here the choice lies between Bouveault's and v. Braun's methods, of which the latter is also suitable for large quantities of material, while Bouveault's method answers only when comparatively small quantities are treated.

The following alcohols prepared by the author are of interest to us in their quality as homologues of phenylethyl alcohol: \(8\)-phenylbutyl alcohol (b. p. 140° at 14 mm.; pronounced, but rather unpleasant odour) \(8\)-phenylamyl alcohol (b. p. 155° at 20 mm.; has a pleasant lemon-like, but rather evanescent odour), \(6\)-phenylhexyl alcohol (b. p. 160 to 161° at 13 mm.; odour similar to that of the phenylamyl alcohol; not particularly pleasant) and \(7\)-phenylheptyl alcohol, a liquid which boils between 170 and 172° (15 mm.) of a faint but particularly agreeable, rose-like aroma.

**Aldehydes.**

*Isocitral.* In our last Report (p. 145) we referred to *isogeraniol*, the alcohol which, according to Semmler and Schossberger, is generated when *enol-citral* acetate is reduced. *Isocitral*, the body corresponding with *isogeraniol*, has been described by Schossberger\(^4\) in his inaugural thesis.

\(^{1}\) Proceed. chem. Soc. 28 (1912), 19

\(^{2}\) Heintz, Liebigs Annalen 122 (1862), 269.


Isocitrinal is left as a residue when reduced enolised citral is treated with phthalic anhydride (for the purpose of isolating isogeraniol), and, when regenerated from the bisulphite-compound, forms a liquid with the following constants: b. p. 103 to 108° (15 mm.), d_{20}^0 0,8976, n_{D} 1,4810. It yields α-isocitryl-β-naphthocinchoninic acid, m. p. 206° (from glacial acetic acid).

Benzaldehyde. For the purpose of preparing the labile benzaldehydepheynylhydrazone discovered by Thiele and Pickard\(^1\), F. B. Thole\(^2\) saturates a suspension of this hydrazone in concentrated hydrochloric acid with hydrogen chloride gas. The resulting red suspension is poured into excess of soda-solution, when the labile benzaldehydepheynylhydrazone is precipitated in the form of a yellowish-white deposit. Recrystallised from glacial acetic acid, it melts at 136°, and when repeatedly recrystallised from this solvent it is gradually transformed into the stable modification, m. p. 152°.

Fatty-aromatic Aldehydes. J. v. Braun and O. Kruber\(^3\) state that in the fatty-aromatic aldehydes, as in the fatty-aromatic alcohols, the odour gradually diminishes in intensity as the polymethylene chain lengthens\(^4\). The authors prepared synthetically a series of fatty-aromatic aldehydes and found that with the majority the methods which have been worked out for preparing these bodies were failures, or yielded poor results. They obtained satisfactory yields, however, by reducing primary nitro-compounds into aldoximes by Konowaloff's method\(^5\), and recovering the aldehydes from the latter by saponification. Thus, for example, for the purpose of preparing the hydrocinnamic aldehyde, γ-iodopropylbenzene and silver nitrite were allowed to react, the result being γ-phenyl-propynitrile and a satisfactory yield of phenylnitropropane. The sodium compound of phenylnitropropane in aqueous solution having been reduced with sub-chloride of tin and hydrochloric acid, the reaction-mixture was neutralised with soda and the resulting hydrocinnamic aldoxime extracted with ether. The best method of isolating the aldehyde is to heat at once with dilute sulphuric acid the residue which remains behind when the ether has been distilled off, after which the aldehyde may be distilled off with steam. Hydrocinnamic aldehyde yields a characteristic diphenylmethane dimethyldihydrazone, m. p. 99 to 100°. Working by the same method the authors obtained the following aldehydes: δ-phenylbutyric aldehyde (b. p. 129 to 131° at 7 mm.; odour fainter than that of hydrocinnamic aldehyde), δ-phenyl-η-valeraldehyde (b. p. 129 to 131° at 10 mm.; odour

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\(^1\) Berl. Berichte 31 (1898), 1250.
\(^2\) Proceed. chem. Soc. 27 (1911), 278.
\(^3\) Berl. Berichte 45 (1912), 384.
\(^4\) Comp. p. 181.
\(^5\) Chem. Zentralbl. 1899, l. 597, 1074.
resembling that of citral), \(\varepsilon\)-phenylcapronic aldehyde (b. p. 141 to 144° at 9 mm.; faint odour), \(\varepsilon\)-phenylöenanthal (b. p. 155 to 159° at 9 mm.; m. p. of the nitrophenylhydrazone 68 to 70°).

Ketones.

W. L. Ipatiew, in collaboration with G. Balatschinsky\(^1\)) has continued his experiments on catalytic reactions at high temperature\(^2\)) and high pressure, and has investigated the course of hydrogenation of unsaturated terpene ketones. The authors reduced \(l\)-carvone, \(d\)-pulegone and \(d\)-menthone with nickel oxide as a catalyst and hydrogen under high pressure at 220 to 280°, and found that hydrogenation is accomplished between 220 and 240°, no matter whether the double bond is in the ring or in the side-chain. The carbonyl-group is attacked between 260 and 280°, but in the case of the menthol series a temperature of 260° must not be exceeded, as otherwise menthane would be formed. The lower the temperature of the reaction, the less is the change in optical rotation. At 280° the reduction of carvone gives rise to carvomenthol, at 240° the double bond is attacked, while the keto-group remains unchanged. At 280° the hydrogenation of pulegone yields menthane, between 220 and 240°, menthone is formed. Menthone at 250° yielded a menthol, m. p. \(-8°\) (d\(_{90}\) 0.8948), which showed some similarity to the menthol obtained by Kondakow and Bachtschiew\(^3\)) in the reduction of diosphenol. It also resembles the menthol (m. p. \(-9°\)) which was obtained in the hydrogenation of thymol at 260°.

Pino lone. The ketone pino lone\(^4\)), a conversion-product of pinol, has been found by Wallach\(^5\)) to be an acetylisopropylcyclopentane. Wallach reduced the pino lone recovered from the semicarbazone by Paal’s method, whereby he obtained a ketone C\(_{19}\)H\(_{18}\)O (dihydropinolone, 1-acetyl-3-isopropylcyclopentane), possessing the following properties: b. p. 211°, d\(_{21}\)0,8880 to 0,8885, n\(_{D21}\)1,4466 to 1,4476. In contradistinction to pino lone, which has a yellow colour, dihydropinolone is colourless; a point of difference which is often found in saturated and in unsaturated ketones\(^6\)). Dihydropinolone semicarbazone melts at 164 to 165°. When dihydropinolone is oxidised with hypobromite liquor there results an acid (1,3-isopropylcyclopentane carboxylic acid), of which the amide, m. p. 164 to 165°, was identical with the body which was obtained by Semmler from camphenilone, and to

\(^{1)}\) Berl. Bericht 44 (1911), 3461.
\(^{2)}\) Comp. Report April 1911, 166.
\(^{3)}\) Journ. f. prakt. Chem. II. 63 (1901), 61; Report April 1901, 71.
\(^{4)}\) Comp. Schimmel’s Bericht, October 1899, 64.
\(^{5)}\) Liebigs Annalen 384 (1911), 193.
which he gave the name of dihydrocamphoceanic acid amide. Bouveault and Blanc have demonstrated that this compound is derived from 1,3-isopropylpentane carboxylic acid. By treating it with bromine and potash liquor this amide was converted by Wallach into the corresponding base, which contains one carbon atom less. This base was converted into the alcohol by treating it with nitrous acid, and the alcohol was oxidised with chromic acid, the result being the ketone 1,3-isopropylcyclodopentanone. (m. p. of the semicarbazon 192 to 193°.) Dihydropinolone was prepared synthetically from 1,3-isopropylcyclodopentanone by treating it with bromopropionic ester. The acid which is generated as the product of the reaction, when submitted to dry distillation, yielded a hydrocarbon, the nitrosochloride of which gave rise to a ketone which was reduced to dihydropinolone by Paal's method. This hydrocarbon, of which the formula probably corresponds in the main with that set forth below, was also prepared synthetically from dihydropinolone. Reduction of this ketone yielded dihydropinolol (b. p. 215 to 216°; d$_{19}$ 0,8920; n$_{D19}$ 1,4569) which, when warmed with chloride of zinc, gave rise to the hydrocarbon which was the object of the experiment (b. p. 171 to 174°; d$_{22}$ 0,812; n$_{D22}$ 1,4515).

According to a communication by W. Bonsdorff the calcium salt of pinic acid, when subjected to dry distillation, does not yield the bicyclic ketone which would be expected, but most probably 1-isopropylene-2-ketopentamethylene. Bonsdorff obtained three fractions, which boiled at 4 mm. between 34 to 50°, 50 to 100° and 100 to 102°. These fractions do not react with semicarbazide-, thiosemicarbazide- or hydroxylamine hydrochlorides, but fraction II, when treated with free semicarbazide yielded a semicarbazon, m. p. 159 to 161°, from which the ketone was regenerated. This ketone boiled between 69 and 71° (8 mm.), its other constants being as follow:

2) Comp. Report April 1908, 191.
3) Berl. Berichte 44 (1911), 3208.
Santenone. According to Rimini\(^1\), the action of nitrous acid upon santenone oxime gives rise to a body possessing all the properties of a pernitroso-derivative; with hydroxylamine and with semicarbazide nitrous oxide is given off, with formation of santenone oxime or semicarbazone. If the body is treated with cold concentrated sulphuric acid, nitrous oxide is also given off, and an unsaturated compound results which yields a semicarbazone, m. p. 180\(^\circ\). The saturated santenone, when subjected to the same treatment, remains unchanged, and also yields a semicarbazone with m. p. 224\(^\circ\); hence the reaction first described had given rise to an isomeride, to which Rimini has given the name of isosantenone. The oxidation- and reduction-products of the new body which have been obtained up to the present hardly bear out the accuracy of Semmler's\(^3\) santenone-formula.

It is expected that Rimini will shortly publish a more detailed paper showing how the process of conversion into an unsaturated body takes place; possibly, as in the case of camphor, there is a rupture of the bridge-formation and an "erection" of the bridge itself.

Menthone. In view of the circumstance that the reduction of menthone in alcoholic solution gives a poor yield, V. Skworzow\(^2\) has reduced this ketone by Sabatier and Senderens' method, but also without obtaining favourable results. Ultimately, however, the following method was found to be effective: the ketone [consisting, in the case under review, of \(l\)-menthone ([\(\alpha\])\(_D\) +14\(^\circ\)) from buchu oil] is dissolved in a brass autoclave in ten times its volume of methyl or ethyl alcohol and treated with more than double the calculated quantity of sodium, in the course of which manipulation the liquid acquires a temperature of between 70 and 80\(^\circ\). The closed autoclave is shaken until the contents have cooled down completely and the reaction-product is then distilled off with steam. The result is a quantitative yield of a mixture of solid ([\(\alpha\])\(_D\) +37,87\(^\circ\) and liquid (\(\alpha\)\(_D\) +16\(^\circ\)) menthol. By the same method the reduction of pulegone (b. p. 222 to 223\(^\circ\); \(d\)\(_{180}\) 0,938; \(\alpha\)\(_D\) +24\(^\circ\)) gives an almost quantitative yield of a mixture of solid and liquid \(l\)-menthol (b. p. 200 to 218\(^\circ\); \(\alpha\)\(_D\) —12\(^\circ\)).

When applied to the reduction of dipentene, pinene, camphene, terpineol, and thymol, the method failed to yield positive results.

On the reduction of menthone, see also p. 183.

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\(2\) Comp. Report October 1910, 120.

\(3\) Journ. f. prakt. Chem. II. 84 (1911), 422.
Some years ago we described Bøedtke-ar's\(^1\) experiments in the action of Grignard's salts upon ethyl- and benzal-menthone, and in our notice we referred among other bodies to menthodiphenylmethane, which occurs in the form of three isomerides. Bøedtke\(^2\) has now oxidised with chromic acid in a glacial acetic acid solution the modifications of menthodiphenyl methane which melt at 140° and between 136 and 137° respectively, and has obtained benzophenone, which proves that the two phenyl groups are found at the same carbon atom.

Bøedtke prepared menthomethylphenylmethane by condensing benzylidene menthone with magnesiummethyl iodide: m. p. 111 to 112°; \([\alpha]_{D190} + 95° 16'\) (in benzene), of which the benzoate melts at 152 to 153°. He also describes menthylisoamyl phenylmethane: b. p. 215° (15 mm.), \([\alpha]_{D20,50} + 13° 45'\) (in benzene solution), which yields a benzoate melting between 93 and 94°.

In conclusion Bøedtke mentions benzoylementhone, a liquid with b. p. 185° (12 mm.) \([\alpha]_{D20,50} + 30° 11'\) in benzene solution, \(n_{D21,80} 1,51745\).

By condensing natural menthone (b. p. 208 to 209°; \(d_{00} 0,8941\); \([\alpha]_{D} - 23,6°\) with magnesium phenyl bromide, M. Murat\(^3\) has prepared the tertiary alcohol methyl-1-phenyl-3-isopropyl-4-cyclohexanol-3: b. p. 175° (20 mm.), \(d_{00} 0,9962\), \(d_{200} 0,9843\), \(n_{D} 1,527\). No phenylurethane was obtained. Treatment of the alcohol with water-eliminating agents (the readiest method being by passing it over aluminium at 300°) gives rise to methyl-1-phenyl-3-isopropyl-4-cyclohexene (b. p. 268 to 272°; \(d_{00} 0,9700\); \(d_{200} 0,9621\); \(n_{D} 1,537\)).

When treated with magnesium cyclohexyl chloride menthone yields methyl-1-cyclohexyl-3-isopropyl-4-cyclohexanol-3 (cyclohexylmenthol) (m. p. 92°), from which, by splitting off water, methyl-1-cyclohexyl-3-isopropyl-4-cyclohexene, results. This hydrocarbon has an odour of garlic and possesses the following constants: b. p. 265°, \([\alpha]_{D} + 6,2°\), \(d_{00} 0,9897\), \(d_{150} 0,9198\), \(n_{D} 1,498\).

Murat has also carried out the reaction of thymomenthone with magnesium phenyl bromide. This ketone, which has b. p. 212°, he prepared by passing thymomenthol over copper heated to 300°. \(i\)-Phenylthymomenthol possesses the following constants: b. p. 170° (18 mm.), \(d_{00} 0,9950\), \(n_{D180} 1,526\). The corresponding menthone boils between 270 and 272°.

The boiling point of \(i\)-cyclohexylthymomenthol, a body which results from the condensation of thymomenthone with cyclohexyl magnesium bromide, is about 164° (15 mm., with partial decomposition): \(d_{00} 0,9931\), \(n_{170} 1,529\). This body yields a cyclohexylthymomenthene with b. p. 260° (756 mm.).

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1) Compt. rend. 145 (1907), 392; Report October 1907, 160.
2) Compt. rend. 154 (1912), 437.
3) Journ. de Pharm. et Chim. 103 (1911), 294.
Camphor. As a result of their investigations, G. L. Blanc and J. F. Thorpe have found that when methyl diketo camphoric acid is reduced by Komppa's method, the methyl-group remains in combination with carbon; from which it follows that their criticism of Komppa's camphoric acid synthesis is without foundation.

Isocamphenilone. If, as is generally assumed to be the case, camphenilone and fenchone are homologues, it would follow (as we gather from a paper by Komppa), that the hydrating of camphenilene (a hydrocarbon which corresponds to camphenilone) would give rise to a new alcohol, differing from camphenilol, and that oxidation of this alcohol would yield a new ketone: isocamphenilone, analogous to the preparation of isofenchyl alcohol from fenchene by Bertram and Helle. As a matter of fact, Komppa, by hydrating camphenilene, obtained a new secondary alcohol C\textsubscript{9}H\textsubscript{15}OH, isocamphenilol (b. p. 196\textdegree at 740 mm.), which he oxidised into isocamphenilone, a ketone with a camphoraceous odour. The best method of obtaining camphenilene is by heating camphenyl chloride with aniline. It possesses the following constants: b. p. 140\textdegree (755 mm.), d\textsubscript{20} 0.8693.

Isofenchone. A good many years ago Bertram and Helle, working in our laboratory upon D-l-fenchene, had prepared therefrom the i-isofenchyl alcohol and from the latter, by oxidation, the ketone C\textsubscript{10}H\textsubscript{16}O, which was subsequently designated isofenchone by Wallach. The last-named investigator, when oxidising isofenchone with permanganate of potassium in alcoholic solution, obtained \textit{l}-isofenchocamphoric acid, in which respect isofenchone is sharply differentiated from fenchone. Aschan has determined the constitution of this acid as follows: 1. The dibasic acid is saturated; both \textit{v}. Bäyer's permanganate test and the bromine-absorption test give negative results; ester-refraction normal. 2. The acid shows a pronounced tendency towards the formation of anhydride. This symptom, together with the fact that when the calcium salt is distilled it does not afford a simple cyclic ketone, indicate a cyclically substituted \textit{cis}-glutaric or succinic acid. 3. The fact that the acid, when heated with a mixture of glacial acetic and hydrochloric acids, is partially convertible into a geometrically isotomic form, \textit{viz.}, trans-isofenchocamphoric acid (m. p. 169 to 170,5\textdegree), shows that the carboxyl which plays a part in the conversion-process is linked directly with the carbon. 4. The \textit{cis}-acid,

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3) Comp. Report October 1909, 198; April 1910, 178; October 1910, 196; April 1911, 182; October 1911, 147.
4) Liebig's Annalen 387 (1912), 293.
5) Journ. f. prakt. Chem. II. 61 (1900), 293; Report April 1900, 56.
6) Comp. Report April 1908, 179.
7) Comp. Report April 1908, 179; November 1908, 190.
8) Liebig's Annalen 387 (1912), 1.
or its chloride, can be readily brominated, giving rise to two geometrically isomeric \( \alpha \)-bromo-iso\( \text{fenchocamphoric} \) acids. But only one bromine atom reacts readily, from which follows that the second carboxyl is linked with the quaternary carbon-atom. 5. The action of bases upon the high-boiling \( \alpha \)-brominated acid gives rise to dehydroiso\( \text{fenchocamphoric} \) acid, indicating that in iso\( \text{fenchocamphoric} \) acid the group \( \text{C} - \text{CH} - \text{CO}_2\text{H} \) is present. 6. The formation of a stable lactone acid (iso\( \text{fenchocamphanic} \) acid) from \( \alpha \)-hydroxy-iso\( \text{fenchocamphoric} \) acid points to the second carboxyl occupying the \( \gamma \)-position towards the hydroxyl of the hydroxy-acid. This hydroxyl is linked to the same cyclic-carbon as is the first-named; hence iso\( \text{fenchocamphoric} \) acid is a cyclically-substituted glutaric acid. 7. Careful melting of iso\( \text{fenchocamphoric} \) acid with potash gives rise to formic acid and to \( \alpha \alpha \alpha \alpha_1 \alpha_1 \)-tetramethyl glutaric acid. 8. In the course of the operation of melting with potash there is formed, in addition to tetramethyl glutaric acid, a keto-acid, which when subjected to further melting, is converted into tetramethyl-glutaric acid. According to Aschan the conversion of the \( \alpha \)-hydroxy-acid during the melting with potash takes place as follows:

\[
\begin{align*}
\text{Isofenchocamphoric acid:} & & \text{a-Hydroxyiso\( \text{fenchocamphoric} \) acid:} \\
\text{H}_3\text{C} & & \text{CH}_3 \\
\text{H}_3\text{C} & & \text{H}_3 \\
\text{H}_2\text{C} & & \text{H}_2\text{C} \\
\text{CO}_2\text{H} & & \text{CO}_2\text{H} \\
\text{CH}_2 & & \text{CH}_2 \\
\text{CH}_3 & & \text{CH}_3 \\
\text{CH}_3 & & \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \xrightarrow{+ \text{H}_2\text{O}} \text{H}_3\text{C} \\
\text{H}_3\text{C} & \xrightarrow{\text{CH}_2} \text{H}_3 \\
\text{H}_2\text{C} & \xrightarrow{\text{CH}_3} \text{H}_2\text{C} \\
\text{CO}_2\text{H} & + \text{H} \cdot \text{CO}_2\text{H} \\
\text{CH}_3 & \text{CO}_2\text{H} \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{a\( \alpha \alpha \alpha \alpha_1 \alpha_1 \)-Tetramethylglutaric acid.}
\end{align*}
\]

\( \beta \)-Pinolene\(^1\), when heated with glacial acetic and sulphuric acid yields iso\( \text{fenchyl} \) alcohol; and is therefore closely allied to this body, as well as to iso\( \text{fenchone} \). In addition to iso\( \text{fenchyl} \) alcohol, the \( \beta \)-pinolene (or cyclo\( \text{fenchene} \), to give it the name proposed by Aschan for the future), yields fenchyl alcohol. The reaction is graphically explained below. The formula for iso\( \text{fenchone} \) assumed by Aschan on the basis of the experimental material collected by him is the same as that which was drawn up by Semmler\(^2\) without any experimental warrant.

\(^1\) Comp. Report October 1909, 169.
\(^2\) Semmler, Die \( \ddot{a} \)therischen \Öle, Vol. III, p. 569.
It would lead us too far to give an explanation of the formation of the fenchene compounds from pinene and of the author's theory of the formation of geometric isomerides in the bromination of dibasic alicyclic acids with hydrogen in the α-position, and in the re-substitution of the α-bromoderivatives. Nor are we able to enter into further details of the rich experimental material.

On the reduction of pulegone, see p. 183.

**Carvone.** When molecular quantities of hydrogen cyanide and carvone are allowed to react at ordinary temperature, the resulting product is cyanodihydrocarvone\(^1\), m. p. 93.5 to 94.5°; \(\left[\alpha\right]_D + 13.5°\). When the reaction is carried out in hot alcoholic solution the result, according to A. Lapworth and V. Steele\(^2\), is an isomeric product, β-cyanodihydrocarvone, m. p. 84° \(\left[\alpha\right]_D - 42.1°\). In the presence of bases this body shows the effect of mutarotation.

When a mixture of carvone hydrosulphide and aqueous solution of potassium cyanide is diluted with glacial acetic acid, the result, as shown by V. Steele\(^3\), is the generation of a dinitrile, with elimination of water. The dinitrile has the following formula p. 190.

It melts at 94°, and has opt. rot. \(\left[\alpha\right]_{D 25°} + 4.02°\) (0.4062 g. substance 25 cc. alcohol). When heated with ferrous hydroxide and alkali it readily loses both its hydrogen sulphide and hydrogen cyanide. When heated with concentrated aqueous hydrobromic acid solution, the nitrile is partly

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\(^1\) Comp. Report October 1906, 132.
\(^2\) Journ. chem. Soc. 99 (1911), 1877.
\(^3\) Proceed. chem. Soc. 27 (1911), 240.
hydrolysed, giving rise to a dibasic acid \((C_{10}H_{14} \cdot CO_2H)_2S\), contaminated with a neutral product.

\[
\begin{align*}
&H_3C \cdot C \cdot CH_3 & H_2C : C \cdot CH_3 \\
&H_2C \cdot C \cdot CH_2 & H_2C \cdot C \cdot CH_2 \\
&CN \cdot C \cdot CH & HC \cdot CH \cdot C \cdot NC \\
&H_3C & CH_3
\end{align*}
\]

In previous Reports (October 1906, 130, 131; November 1908, 186) we have discussed the investigations of Rupe and Liechtenhan, of Klages and Sommer, and of Rupe and Emmerich into the hydrocarbon methylmenthatriene, which is generated by treating carvone with magnesium methyl iodide. Rupe and Kerkovius\(^1\) have further pursued these investigations and have prepared a hydrocarbon of greater stability than methyl menthatriene, namely tetramethyl cycloheptatriene, which is readily obtainable from eucarvone and magnesium methyl iodide. The first product is a tertiary alcohol which gives off water at water-bath temperature and is converted into the hydrocarbon. The latter forms a very mobile liquid, with an odour reminding first of camphor and then of cajuput oil: \(b. p. 67\) to \(68^\circ\) (11 mm.), \(d_{20}^0 0.8687, n_{D20}^0 1.50660\). When reduced with alcohol and sodium it yields tetramethyl cycloheptadiene.

A modification of the process by allowing eucarvone and methyl iodide to flow on to the magnesium, yields, in addition to the hydrocarbon, two solid bodies, m. p. respectively 177 to \(178^\circ\) and 142 to \(143^\circ\). These bodies are probably stereomeric and represent dimolecular methyl derivatives of dihydroeucarvone.

**Phenols.**

**Dicarvacrol.** On p. 200 of our Report of October 1910 we referred to dehydrodicarvacrol (dicarvacrol), a body which has been obtained by Cousin and Hérissey by acting with ferric chloride upon an aqueous carvacrol solution. Since then, Cousin\(^2\) has investigated the action of bromine and chlorine upon dehydrodicarvacrol and has described a few well-defined halogen-compounds.

**Oxides.**

**Cineole.** G. Cohn\(^3\) has established that cineole combines with 1,5-dihydroxy-naphthalene to form a double-compound which crystallises in the

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1\) Berl. Berichte 44 (1911), 2702.
2\) Compt. rend. 154 (1912), 441.
3\) Pharm. Zentralh. 58 (1912), 32.
form of beautiful yellow needles, and which may be readily split up into its constituents by alkalies. He has also observed that coumaric acid readily reacts with cineole under heat, forming a double compound from which cineole can be immediately regenerated by treatment with soda liquor.

**Acids.**

*Camphocarboxylic acid.* Camphocarboxylic acid, which is not reducible by the usual methods, may, as discovered by Bredt in collaboration with Burkheiser and Sandkuhl\(^1\), be reduced to borneol carboxylic acid by the electrolytic method. According to Bredt\(^2\), camphononic acid behaves similarly, being electrically reducible to camphonolic acid (di-hydrocamphononic acid). The camphononic acid was prepared by the modified Lapworth-and-Lenton method, by preparing free hydroxycamphor-aminic acid from camphanic acid amide, and submitting the sodium salt of this acid to Hofmann's reaction with exactly determined quantities of bromine and alkali. The actual yield averaged from 67 to 69\(^{\circ}/\) of the theoretical. 10 grams camphononic acid electrically reduced yielded 9 grams reduction-product, containing 4.5 grams camphonololactone, the remainder consisting of *cis-trans*-camphonolic acid and of unattacked camphononic acid. The camphonololactone boils at 239,2\(^{\circ}\) and melts between 160 and 161\(^{\circ}\). Boiling of the lactone with aqueous barya solution afforded *cis*-camphonolate of barium, from which the free hydroxy acid was separated with hydrochloric acid by cooling in ice. This body has no true melting-point, being partly converted, when heated, into the lactone, owing to elimination of water. The *cis-trans*-camphonolic acid which was isolated from the reduction-mixture by extraction with soda solution formed bunches of crystals, m. p. 249 to 250\(^{\circ}\).

Camphononic acid can be reduced with sodium amalgam without the aid of the electric current, but in this case the reaction is exceedingly slow. With 30 grams acid it required over 50 hours, the amalgam having to be renewed no fewer than seven times, 1000 grams being taken up each time. When the camphonololactone is shaken with saturated hydrobromic acid, \(\gamma\)-bromo camphonic acid (m. p. 146 to 147\(^{\circ}\)) is formed. When the camphonololactone and the *cis-trans*-camphonolic acid are oxidised with nitric acid camphoronic acid is generated.

*Bornylene carboxylic acid.* A few years ago, Bredt and Sandkuhl\(^3\) had made the remarkable discovery that hydrobromic acid reacts with bornylene carboxylic acid, giving rise to various bodies according to whether the reaction is carried out in an aqueous or in an anhydrous

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\(^1\) Comp. Report October 1906, 135; Report October 1909, 192.

\(^2\) Journ. f. prakt. Chem. II. 84 (1911), 786.

\(^3\) Liebigs Annalen 866 (1909), 39; Report October 1909, 194.
solution. In the latter case the reaction usually takes a normal course. Basing themselves upon the results thus obtained, Bredt and Sandkuhl\(^1\), for the purpose of preparing the \(\beta\)-hydriodo-bornylene carboxylic acid solution, saturated the bornylene carboxylic acid in a solution of glacial acetic acid with hydriodic acid. The free \(\beta\)-hydriodo-bornylene carboxylic acid occurs in beautiful needle-shaped crystals, m. p. 129 to 130°. Its sodium salt, in analogy with \(\beta\)-hydrobromo-bornylene carboxylic acid, yields, when boiled with soda-liquor, bornylene carboxylic acid together with small proportions of bornylene (m. p. 113°; b. p. 146° at 745,5 mm.; \([\alpha]_{D20} = -23,68^\circ\) in toluene solution). When heated with glacial acetic acid + sulphuric acid, bornylene yields a body with an odour reminding of \(\text{iso}\)bornyl acetate, b. p. 103 to 104° (14 mm.) which upon saponification afforded a borneol with a not very sharp m. p.

Bornylene carboxylic acid yields a dibromo-derivative, m. p. 159 to 160°. When \(\beta\)-hydriodo-bornylene carboxylic acid is reduced it yields hydro-bornylene carboxylic acid (b. p. 171° at 22 mm.). The chloride boils between 114 and 115° (14 mm.), and the amide has m. p. 166 to 167°.

Cinnamic Acid. Several detailed investigations into the conditions of isomerism in cinnamic acid have again been published, and to these we will briefly refer in connection with our previous notes\(^3\). E. Erlenmeyer\(^3\) in his paper on labile interconvertible isomerides of similar structure, discusses the conditions of isomerism which have been observed in the various cinnamic acids. Investigation of the labile cinnamic acids of the \(\text{iso}\)-series showed that here we have to deal with cases of isomerism which cannot be explained either by the atomic structure or stereo-chemically, and of which the differences must be assigned to a still unknown difference in the position of some parts or other of the molecules. Although the lability of the acids is not so great as to cause the differences in the modifications to disappear in the melting, it would yet seem that certain conditions exist in which the lability is very considerable, and this explains why Stobbe\(^4\) (see p.195) in one case obtained from the three acids solutions in which by his experimental method he was unable to detect any differences. The conditions referred to above, however, cannot as yet be experimentally determined. In forming a judgment of the conditions of isomerism which exist in this case the fact is of great importance that the \(\text{allo}\)-acid, by being brought under the influence of heat, is finally converted into the most labile of all acids, — the \(\text{iso}\)-acid of Erlenmeyer sen. The

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\(^1\) Journ. f. prakt. Chem. II. 84 (1911), 778.

\(^2\) Comp. Report April 1907, 155; April 1909, 138; October 1909, 210: April 1910, 188; October 1910, 203.

\(^3\) Biochem. Zeitschr. 34 (1911), 306. Copies of this and the other reprints here referred to were kindly sent to us by the authors.

\(^4\) Berl. Berichte 43 (1911), 506.
last-named acid must be regarded as being the most labile and the richest in energy, and the allo-acid as the most stable and the most deficient in energy. Between the two stands Liebermann's iso-acid.

A second paper by Erlenmeyer¹) deals with the isomeric acids of the cinnamic acid series. It has been demonstrated by various methods that synthetic cinnamic acid is a uniform crystallising mixture of storacic and hetero-cinnamic acids. But, as we have already mentioned in previous references to the matter, the objection has been raised that the difference between hetero- and storacic-cinnamic acid may have been caused by some impurity in the hetero-cinnamic acid. It is scarcely possible, in certain circumstances, to invalidate this objection, especially if it be assumed that the impurity is so small as to be no longer detectable by the available methods. In order to disprove this hypothesis of contamination, Erlenmeyer has made a symposium of the differences which have been found to exist in the past and recently between storacic and synthetic cinnamic acids on the one hand and storacic and hetero-cinnamic acids on the other. He has next described two methods by which it is possible to give convincing proof of the structural identity of storacic and hetero-cinnamic acids.

In common with cinnamic acid, benzaldehyde also appears to occur in several modifications. From the detailed communications by Erlenmeyer, G. Hilgendorff and T. Marx²) on separation and conversion in the benzaldehydes we abstract the following particulars: In Perkin's reaction the natural benzaldehyde, before being deprived of its hydrocyanic acid, gives rise to storacic-cinnamic acid, and after the elimination of hydrocyanic acid, to synthetic, and in some cases to hetero-cinnamic acid. The behaviour of the natural benzaldehyde before and after being deprived of its hydrocyanic acid is very different, not only under condensation but also under distillation. It would appear that natural benzaldehyde before the abstraction of its hydrocyanic acid consists principally of storacic benzaldehyde, whereas benzaldehyde deprived of its hydrocyanic acid is composed of a mixture of storacic and hetero-benzaldehydes, from which under condensation synthetic cinnamic acid is generated. But it is not possible to base upon the distillation a method of separating the various benzaldehydes. The conditions are more favourable when the separation, which is based upon the varying rates of velocity of the reaction, is taken as the basis, but this method has the disadvantage that only one of the two components can be recovered, as the other undergoes a change in the course of the reaction. Erlenmeyer looks for the causes of the differences in the cinnamic acids and benzaldehydes in the benzene-nucleus itself, and it is to be assumed with v. Baeyer that it is possible for the benzene

²) Biochem. Zeitschr. 34 (1911), 386.
nucleus to exist under conditions of different stability which are susceptible of inter-conversion.

According to Erlenmeyer the esters of cinnamic acid and the benzaldehydes may be differentiated by their odour by those who have acquired some experience in this field of investigation. Of the two benzaldehydes, for instance, hetero-benzaldehyde has a much more acrid odour than storacic benzaldehyde, of which the odour is bland.

The detection of the differences in the properties of the cinnamic acids and benzaldehydes to which reference is made above has induced the authors to extend their research to the investigation of benzene and stilbene, and here they discovered similar differences as in the benzaldehydes. Other differences, such as the formation of various derivatives and differences in the rates of velocity of reaction cannot, according to Erlenmeyer, be expected in isomerides of identical atomic structure. These isomerides however, must be distinguished by differences in energy.

In order to discover whether the peculiar behaviour of the cinnamic acids may perhaps be due to impurities arising from derivatives, Erlenmeyer and Hilgendorff1) have prepared mixtures of storacic cinnamic acid with various such derivatives. They examined mixtures with \(p\)-, \(o\)-, and \(m\)-chlorocinnamic acid, with \(p\)-, \(m\)-, and \(o\)-hydroxy-cinnamic acid, with \(o\)- and \(p\)-methoxy-cinnamic acid and with methyl-cinnamic acids. Among all the mixtures which were prepared by the authors that consisting of 1 part \(p\)-methyl-cinnamic acid and 99 parts storacic cinnamic acid resembles synthetic cinnamic acid to a quite extraordinary degree, but the presence of this acid may be proved beyond doubt by oxidation and separation of the terephthalic acid. Attempts at oxidation with heterocinnamic acid afforded no trace of terephthalic acid. When a mixture contains 10\% methyl-cinnamic acid that body may be removed by fractional precipitation, but a 20\% content of methyl-cinnamic acid cannot be detected by combustion. The result of the crystallographic examination of the various mixtures was that of all the admixtures recorded above only that with methyl-cinnamic acid makes a mixture with any resemblance to synthetic cinnamic acid.

So far it had not been established whether the two constituents, storacic and hetero-cinnamic acids, which have been separated out from synthetic cinnamic acid could be further split up. The results of investigations into this subject which have been carried out by Erlenmeyer and G. Hilgendorff2) agree that synthetic cinnamic acid prepared from chlorine-free benzaldehyde or from natural bitter almond oil free from hydrocyanic acid, does not owe such of its properties as differ from those of storacic cinnamic acid to any impurity, but that it consists of a mixture of storacic cinnamic acid and hetero-cinnamic acid which crystallise together.

1) Biochem. Zeitschr. 34 (1912), 405.
In conclusion, Erlenmeyer and Hilgendorff ¹), and Erlenmeyer ²), in connection with the investigations mentioned above, engage in theoretical considerations of the problem whether molecular asymmetric storacic cinnamic acids can exist, and of isomerism in ethylene derivatives. We regret that considerations of space compel us to restrict ourselves to a bare mention of these interesting questions.

The chlorine-free benzaldehyde, and part of the natural bitter almond oil used in these investigations had been placed at the authors’ disposal by us.

Some further reference must also be made to the researches of H. Stobbe and F. Reuss ³), and of Stobbe ⁴). Stobbe and Reuss investigated the optical refraction of the melted acids and discovered that in a range of temperature of about 50° the melttings of allo- and isocinnamic acids have the same refraction and that therefore they must be regarded as optically identical. Stobbe (loc. cit.) has further occupied himself with the conversions of the allo- and isocinnamic acids in the flux and in the crystalline form. His conclusion is that there exist two different isomeric cinnamic acids, viz., monomorphous allocinnamic acid (m. p. 68°) and dimorphous isocinnamic acid (m. p. 58° and 42°). This so-called-conclusion appears to him to afford the best summary of the allo- and isocinnamic acid question, taking also into account the results obtained by all other investigators.

According to Meyer ⁵), the researches of Stobbe do not supply sufficient experimental material to warrant the adoption of the theory of chemical isomerism between the allocinnamic acid with m. p. 68° on the one hand and the acids melting at 58 and 42° on the other.

Finally, H. R. Kruyt ⁶) controverts not only Stobbe but also Meyer’s criticism of the latter.

Nitrogenous bodies.

According to N. Kishner ⁷) hydrazine compounds are capable of being resolved into hydrocarbons and nitrogen by boiling them with solid potassium hydroxide. Thus, 1,3-methylocyclohexylidene hydrazine yields methylcyclohexane; camphylidene hydrazine (m. p. 53 to 55°) yields camphane (m. p. 158 to 159°); fenchylidene hydrazine yields fenchane (b. p. 151,5°) and cyclohexylidene hydrazine hydrate yields cyclohexane. The dihydro-

¹) Biochem. Zeitschr. 85 (1912), 134.
²) Ibidem 149.
³) Berl. Berichte 44 (1911), 2735.
⁴) Ibidem 2739.
⁵) Ibidem 2966.
⁶) Ibidem 3108.
carvone hydrazine compound affords \( \Delta^{8.9} \)-menthene (b. p. 170°). With fuming hydrobromic acid, \( \Delta^{8.9} \)-menthene yields a bromide which, upon being boiled with aniline, affords \( \Delta^{4.8} \)-menthene (b. p. 170.5 to 172.5°), and with 20% sulphuric acid, \( \Delta^3 \)-menthene. The carvenone hydrazide compound, when heated with solid potassium hydroxide, yields \( \Delta^3 \)-menthene. The citronellal hydrazine compound yields a hydrocarbon \( \text{C}_{10} \text{H}_{18} \), b. p. 164.5°. The hydrazine compound of citral gives rise to a hydrocarbon \( \text{C}_{10} \text{H}_{18} \) (b. p. 164 to 165°).

v. Baeyer assumes that the relation of bisnitrosyl carone towards carone bisnitrosyl acid, which is obtained by treating the first-named body with hydrochloric or sulphuric acid, corresponds to the relation of ether to alcohol. Bamberger\(^1\), however, takes another view of the conversion. He argues from the known fact that all the \( C \)-nitroso bodies are capable of forming monomolecular solutions, and that the bimolecular forms are less energetic than the monomolecular forms. The last-named he regards as the reactions of all \( C \)-nitroso compounds, including the bisnitrositised. In his opinion the conversion of bisnitrosylcarone yields first monomolecular nitrosyl carone, which latter is split up by the action of hydrogen chloride into chlorocarone and Angeli’s nitroxy!e. The latter, with a second molecule of nitrosocarone, affords carone bisnitrosyl acid (carone nitrosohydroxylamine, the conversion proceeding as follows:

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\begin{align*}
\text{C}_{10} \text{H}_{18} \cdot \text{NO} & + \text{HCl} = \text{C}_{10} \text{H}_{18} \cdot \text{Cl} + \text{NOH} \\
\text{C}_{10} \text{H}_{18} \cdot \text{NO} & + \text{NOH} = \text{C}_{10} \text{H}_{18} \cdot \text{N} + \text{OH} \\
\end{align*}
\]

Bamberger’s views are based upon observations made by him in v. Baeyer’s own researches on the conversions: bisnitrosyl menthone \( \rightarrow \) menthone-bisnitrosyl acid and chloromenthone, and bisnitroso pulegone \( \rightarrow \) pulegone-bisnitrosyl acid and chloropulegone. The change in colour which is observed when a solution of \( \text{i} \text{so} \text{safrol-} \) or anethol pseudonitrosite is alternately warmed and cooled down in glacial acetic acid, benzene or chloroform, is attributed by Bamberger to a manifestation of desmotropy, but he does not oppose the view that, in the main, a decomposition of a different kind takes place when the solutions are warmed.

**Dihydrocarvylamine.** According to G. F. Morrell\(^2\), when an ethereal solution of dihydrocarvylamine is saturated with hydrochloric acid gas, the result is a chlorinated base, chlorotetrahydrocarvylamine (m. p. 205°), which, when heated with pyridine, yields a mixture of \( \alpha \)- and \( \beta \)-dihydroterpenylamine. Both bodies are difficult to obtain in the pure

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1\(^\) Berl. Berichte 44 (1911), 3066.
2\(^\) Berl. Berichte 44 (1911), 2560.
state. Benzoyl-α-dihydroterpenylamine has m. p. 219°, and when ozonised yields 2-benzoylamino-1-methylcyclohexanone-4 and acetone, which fact elucidates the constitution of dihydroterpenylamine. Benzoyl-β-dihydroterpenylamine melts between 178° and 179°.

Benzoyldihyrocarylylamine, when treated with ozone, is converted into 1-methyl-2-benzoylamino-4-ethanoylcyclohexane.

On the occurrence of indole in *Citrus*-flowers, see p. 165.
Schimmel & Co.'s Printing Office, Miltitz near Leipzig.