SEMI-ANNUAL REPORT
on
Essential Oils,
Synthetic Perfumes, &c.
Published by

SCHIMMEL & CO
(Fritzsche Brothers)

MILTITZ
near Leipzig

LONDON — NEW YORK

APRIL 1913.
In memoriam.

It is our sorrowful duty to refer once more to the sudden bereavement our New-York branch has suffered in the unexpected death of

Mr. Carl Brucker,

our senior resident partner in that city. We need not enlarge on the important part the deceased has played in the development of our American business, with which he was connected for nearly 20 years. His affability and genial disposition were highly appreciated by the many friends who mourn with us his untimely death.

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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°.
$\alpha_{D20^\circ}$ = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
n$_{D20^\circ}$ = 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.
Notwithstanding its warlike guise, the year 1912 has again brought ample successes to German industry, and the statistical data now before us indicate a continued development of such magnitude as perhaps no one would have thought possible in view of the course of events in the Balkans, and of the fact that the friendly relationships between the great Powers of Europe were at times disturbed to a critically dangerous point. The world's commerce has increased to an extent far exceeding its average yearly growth during the last decade. The value of the imports of commodities into almost all European countries has risen; Russia and France alone show a decrease. The prosperous condition of German industries in general, and foremost among them of the chemical industry, has been even more clearly in evidence than was the case in the two years immediately preceding. There can be no doubt that the mainspring of this exceptionally favourable development (a development which the warlike operations themselves were powerless to check) was the bountiful harvests throughout the world. Everywhere the plenteous yield of the crops increased the purchasing power of the agricultural classes, with the result that all products of industry were in strong demand. Another cause, and one which has powerfully helped to the advance of the world's trade, was the exceedingly satisfactory development of certain oversea markets, such as Argentina, Brazil, Canada, Japan and others. The importance of these markets is steadily on the increase. The enhanced output of gold, especially in South Africa, has been another favourable factor. Those events of the year 1912 which have disturbed the economic life of nations may be briefly summarised as follows: — the Italo-Turkish war, lasting until October; the outbreak of the as yet unfinished Balkan war and the tension between Austria and Russia which, had it spread to the neighbouring and allied Powers, would have meant danger of a European war. It is due to the cool commonsense of the Governments concerned that the torch of war has not been carried into the territories of the Great Powers and that at the present moment we are able to look to the future with far greater confidence than was possible a few months ago. Only the future, however, can reveal whether the Balkan war will have for its sequel a turn in the favourable tide of the markets, or whether it will only result in their temporary weakening, followed by a renewed improvement as soon as the warlike operations have reached a close, a consummation which, it is to be hoped, may soon come to pass. To what extent the treasure of Peace is valued by the German nation is shown by the unanimity with which Germany is preparing to find the means to defray the cost of increased armaments, the necessity for which is thoroughly appreciated by all classes of the German people.

Closely connected with the political events, and with the dangers that threaten the economic structure of society, was the convulsion of the Exchanges and of the

1) The Introduction to the present Report, and the Commercial part, were written in the month of March.
money-market, which attained a degree of acuteness unknown for many years. There were times when the want of commonsense of the public almost threatened disaster, and it was not until towards the end of the year that a certain degree of calmness was restored. The Syndics of the Commercial Community of Berlin publish the following remarks on this subject in the Berliner Jahrbuch für Industrie: "Under the influence of the industrial boom, and afterwards of the uncertain political situation, the Imperial Bank has been put to a heavy strain during the greater part of the year 1912. It was a considerable achievement, both politically and economically, that the Imperial Bank was successful in getting through the month of September without raising its rate of discount, which was maintained at 4½ p.c., and this in a year of strong industrial activity and stock-exchange movement, in which moreover the German money-market was in the main left to depend upon its own resources. If the political situation had developed quietly, the Imperial Bank would in all probability have succeeded in maintaining the same rate to the end of the year".

If one considers that owing to the withdrawal from Germany, after the Morocco crisis, of nearly all the balances due by her to foreign, especially French, creditors, the German money-market was left to depend upon its own strength alone, one feels bound to endorse without reserve the acknowledgment of the services rendered by our Imperial financial institution. Unfortunately, events compelled the Imperial Bank to raise its discount-rate on 24th October to 5 p.c. and on 14th November to 6 p.c., because the prospects of a disturbance of peace caused the public to take the most pessimistic view of the situation, and because the demand for money was steadily on the increase.

The following figures show the totals of the foreign trade of Germany during the past year:

<table>
<thead>
<tr>
<th></th>
<th>Imports 714,000,000 Double cwt. (of 100 kilos) value 10,330 Million Marks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compared with</td>
<td></td>
</tr>
<tr>
<td>1911 684,000,000</td>
<td>&quot; &quot; &quot; 100 &quot; &quot; 9,544 &quot; &quot;</td>
</tr>
<tr>
<td>Exports 655,000,000</td>
<td>&quot; &quot; &quot; 100 &quot; &quot; 8,900 &quot; &quot;</td>
</tr>
<tr>
<td>Compared with</td>
<td></td>
</tr>
<tr>
<td>1911 591,000,000</td>
<td>&quot; &quot; &quot; 100 &quot; &quot; 8,100 &quot; &quot;</td>
</tr>
</tbody>
</table>

The share of the world's commerce of the other two principal European trading nations was as follows:

<table>
<thead>
<tr>
<th></th>
<th>U. Kingdom Imports 14,897 Million Marks, Exports 11,985 Million Marks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1911</td>
<td>&quot; 13,815 &quot; &quot; 9,222 &quot; )</td>
</tr>
<tr>
<td>France . . .</td>
<td>&quot; 6,427,1 &quot; &quot; 5,385,6 &quot; )</td>
</tr>
<tr>
<td>(1911</td>
<td>&quot; 6,529 &quot; &quot; 4,938 &quot; )</td>
</tr>
</tbody>
</table>

These statistics show that the values for the United Kingdom constitute a record and take the first place both as regards the total and as regards the percentage of increase. On the other hand, the value of French imports shows a considerable decrease as compared with 1911, a fact which is due in the first place to the diminution of her imports of agricultural produce. The falling-off equals about £ 13,000,000.

Our German industry of essential oils and synthetics has been very fully occupied throughout the year, and the, at times very serious, danger of war scarcely seemed to exercise any restrictive influence upon its activity. Apart from this, the prevalence of favourable conditions contributed to the extraordinary animation of business in certain departments. The diminution in turnover due to the temporary effacement of the markets in the Balkan peninsula was more than outweighed (as stated above), by

2) 1912, l. 5.
the increased orders from oversea markets as a result of their greatly enhanced purchasing power. This subject is dealt with in detail in our references to those particular countries.

It is true that the difficulties which have been placed in the way of the shipment of our commodities have not yet been legally removed since our last Report was published, but the Commissions which have been appointed to draw up proposals of settlement are hard at work, and the final and satisfactory solution of this serious problem may therefore shortly be expected.

The subjoined figures show the imports and exports of essential oils\(^1\) into and from Germany during the last six years:

<table>
<thead>
<tr>
<th>Year</th>
<th>Imports (Kilos)</th>
<th>Exports (Kilos)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>1,578,400</td>
<td>711,300</td>
</tr>
<tr>
<td>1911</td>
<td>1,251,200</td>
<td>599,300</td>
</tr>
<tr>
<td>1910</td>
<td>1,524,300</td>
<td>549,700</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>

The foreign trade of Germany in synthetics\(^2\) during the past five years was as follows:

<table>
<thead>
<tr>
<th>Year</th>
<th>Imports (Kilos)</th>
<th>Exports (Kilos)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>18,400</td>
<td>574,800</td>
</tr>
<tr>
<td>1911</td>
<td>17,300</td>
<td>492,800</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>
</tbody>
</table>

It will be seen from the above figures that in our industry the exchange of commodities with foreign countries has made considerable progress in all directions in the year 1912. This applies especially to the export trade, in which even the German record-year 1907 was left far behind.

Although the situation of the spirit-industry of Austria-Hungary does not as yet display any noticeable improvement, and in spite of the fact that the struggle with the Spirit-Trust, to which reference was made in our last Report, is still in progress, we have no reason whatever to complain of the amount of sales of our manufactures effected by our branch-factory of Bodenburg, our turnover there again showing an important advance on that of the year 1911. The new law on the taxation of spirit, which will inflict a burden upon all branches of industry in which alcohol is used, was planned to come into force on March 1\(^{st}\), but the date of its entering into operation has again had to be postponed, because it was found impossible to carry the so-called "Minor Financial Scheme" through the House of Representatives before Easter. It is now probable that the introduction of the increased spirit-tax will be delayed until September 1\(^{st}\), when the manufacturing season opens, because an earlier enforcement would cause technical difficulties of administration. We understand that it is contemplated to increase the excise-duty payable upon alcohol from 0,90 to 1,40 Kronen per hectoliter. So far as we are able to form a judgment of the state of the soap- and perfumery-industries in Austria from the orders received by us, this branch has continued to make good progress, in spite of the general complaints of keen competition and low rates of profit. In view of the serious increase in the cost of raw materials during the past year, the Austrian toilet-soap and perfumery manufacturers

\(^1\) Statistisches Warenverzeichnis, No. 353 b/c.  
\(^2\) Statistisches Warenverzeichnis, No. 354.
have combined to advance by 5 p.c. all round, as from January 1st, 1913, the prices of soaps, perfumes, tooth-pastes, cosmetics, &c.

The provisional statistics relating to the foreign trade of the Monarchy\(^1\), which have just been published, show an increase in the value of imports of 295,3 million Kronen (the total being 3487,2 million Kronen), and those of the exports of 257,6 million Kronen (the total being 2661,9 million Kronen). The total turnover, therefore, advanced in round figures by 553 million Kronen, and the aggregate exceeded 6000 million Kronen. As the increase in the imports exceeds that of the exports by 37,7 million Kronen, the excess of imports over exports for the year shows a further growth to this amount, and is now 825,3 million Kronen as compared with 787,4 million Kronen in the year 1911. The Ministry of Commerce, however, points out that the figures for the year 1912 are only provisional, and that in estimating the values for that year the prices of the year 1911 have generally speaking been taken as a preliminary basis, with the exception of a few important articles to which the new scale of prices for 1912 has already been applied. Moreover, the figures at present published refer merely to "special" trade, and it is quite possible that when the totals relating to the industry of finished articles (which every year shows a not inconsiderable balance on the export side) are available, the commercial balance of the Empire may appear in a somewhat more favourable light.

The import- and export-values of the three principal divisions of commercial commodities, as compared with the previous year, are as follows:—

<table>
<thead>
<tr>
<th></th>
<th>Imports Millions of Kronen</th>
<th>Exports Millions of Kronen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1912 comp. with 1911</td>
<td>1912 comp. with 1911</td>
</tr>
<tr>
<td>Raw materials</td>
<td>1963,8 + 132,7</td>
<td>960,0 + 142,4</td>
</tr>
<tr>
<td>Semi-manufactures</td>
<td>567,1 + 82,4</td>
<td>505,0 + 44,1</td>
</tr>
<tr>
<td>Finished manuf.</td>
<td>956,4 + 80,4</td>
<td>1196,8 + 71,1</td>
</tr>
</tbody>
</table>

It will be observed that in each of these three divisions there has been an increase, both in imports and exports. In the case of raw materials the increase in exports exceeds that of the imports, whereas in the case of semi-manufactures and of finished articles the rate of increase of imports continues to be greater than that of exports. If a balance is struck in the three divisions, it will be seen that the traffic in raw materials shows an excess of imports over exports of more than 1000 million Kronen; whereas that in semi-manufactures shows a surplus of imports of, say, 52 million Kronen, the traffic in finished manufactures alone exhibiting an excess of exports over imports, to the extent of 240 million Kronen in round figures. Taking the commercial balance all round, therefore, the great excess of imports over exports continues to be due principally to the excess of imports of raw materials.

The sale of our productions to France has made another considerable step in advance during in the past year, especially in the winter months. We see in this fact a welcome proof that the systematic outcry against German manufactures which has lately been raised in the chauvinistic press of our Western neighbours is not approved in those circles which are our criterion for estimating the state of our relations with the Republic. Far be it from us to maintain that our German newspapers are free from the besetting sin of Jingoism, but it is a fact that, especially quite recently, French press-attacks upon Germany have reached an extreme which any impartial reader, no matter what may be his nationality, must admit to be unworthy of the press of a civilised people. The recently-published returns of the French Customs

\(^1\) *Handelsmuseum*, XXVIII, 6.
Administration for the year 1912 show clearly that there is no cause whatever for any fear of an economic invasion allemande, seeing that these returns show the value of imports into France from Germany to be 981 million francs, and that of French exports to Germany as 814 million francs. These figures indicate that French purchases from Germany have increased by 2000000 francs only, whereas French sales to Germany have risen by over 20000000 francs. We ask ourselves in vain what may be the cause of the French misgivings, and we can only regard it as a not very tactful and extremely short-sighted proceeding on the part of a section of the French press to do its best to bring about the forfeiture of the sympathy of such a valuable market as Germany, in effect, constitutes. For it must be remembered that Germany, as a market for French goods, is only surpassed in importance by Great Britain and by Belgium, and that now-a-days, to quote only one example, the value of French exports to such an important consuming country as the United States barely reaches one-half of that of the French exports to Germany. In commenting upon these matters the Petite République draws certain conclusions of which we append a translation, by way of conclusive proof that public opinion in France is by no means unanimous in approval of the German-baiting tone which has lately been adopted in many quarters in the Republic. "There is a danger", says the Petite République1) "that just at a moment when the tendency of commercial interchange between the two countries is beginning to show a change in favour of France, at the very moment when Germany, enriched by the development of her great industries, is about to become one of the most valuable markets for our articles de luxe (the only market, in fact, in which we stand without a competition), this movement may be impeded by heedless attacks which must of necessity lead to reprisals. How much more fruitful than this would be a healthy commercial rivalry in which our producers, our traders and our manufacturers would make it their endeavour to beat Germany in the domain of commerce, not by trying to set up artificial barriers against German products by inciting people against Germany, but by adopting the more rational commercial methods of Germany, by organising French export trade, and by putting the same energy into the conquest of the German market which the Germans show in trying to gain a footing in France. Moreover, it should not be forgotten that the interweaving of interests, the logical sequel of commercial development, would form one of the greatest guarantees of enduring peace between the two nations, a guarantee at least as great as any diplomatic understanding!"

The past six months have failed to bring about any clearing up of the political situation in the United Kingdom. There is little doubt that a great deal of water will flow under London Bridge before the present condition of embitterment between the opposing political parties gives way to an era of calm co-operation. It is true that the Home Rule Bill recently passed its third reading in the House of Commons without much difficulty, but a few weeks afterwards it was rejected by the House of Lords with equal determination. This is equivalent to its early re-introduction into the House of Commons, and to a consequent revival of the political agitation of recent years, unless in the meantime a change of Government should supervene.

The strikes and other disturbances among the labouring classes which are incessantly breaking out, now here now there, in almost all branches of British trade and industry, also constitute a grave economic impediment. Upon thousands and thousands of workmen (many of them only indirectly concerned in the dispute at issue) and their generally numerous families, the immediate effect is hunger and misery; in

1) Deutsche Export-Revue V. 12.
capitalistic circles the unavoidable sequence is the feeling of unsettlement and consequent abstention from new ventures. Unfortunately it would seem that the Government, the Chambers of Commerce and other mediatory authorities are almost powerless in the face of these upheavals, which have become distressingly regular incidents in British life of recent years. But the gravest sign of all is that the labour-leaders themselves are no longer able to count upon discipline among their followers, for during the last few years several strikes have been declared, mostly on the railways, against the expressed wish of the leaders. Some of these strikes have only lasted a couple of days, or at most a few weeks. One of the many causes of these events may perhaps be sought in the steady increase in the price of the necessities of life, which has become more and more marked in recent years, although not perhaps to the same extent as has been the case in most countries where a high protective policy prevails.

Notwithstanding these and other unfavourable signs, business generally has been very good in the British Isles, so that, speaking purely from a commercial standpoint, the year 1912 may fitly be described as a record year. The official Board of Trade Returns of imports and exports have shown steadily increasing figures, and, as was to be expected, the totals for the year were the largest ever attained. Our London branch has enjoyed its fair share of the brisk trade and has been very fully occupied throughout the year.

The unsettlement and depression of the general European situation have made themselves felt in Spain more than in any other country; hence during the last few months the course of business in that country has been extremely dragging in all branches. The effect of these external influences has been aggravated by the unsatisfactory condition of Spanish politics. Within the last few months the Liberals, the governing party in recent years, have become leaderless. In the month of November the Prime Minister, Sr. Canalejas, who at last, after lengthy preparatory labours, had just arrived at the beginning of the realisation of his true programme, fell a victim to an anarchist attempt upon his life, and his death has left many of his plans and projects unfulfilled. Then, only a few weeks ago, the death occurred of the other leader of the Liberal party, the gifted Sr. Moret. Although up to the present the Liberals have succeeded in maintaining the reins of Government and have been successful in resisting all Conservative attempts to oust them, it is impossible to foresee which party will be victorious and what aspect the Spanish political situation will assume in the immediate future. Naturally all these internal broils are not conducive to the improvement of trade and traffic.

There has been a good deal of talk lately of a possible abandonment by Spain of its attitude of aloofness from European politics, and it is said that she is hesitating between joining the Triple Alliance or the Triple Entente. In view of the influence of Britain at the Spanish Court the chances of Spain coming to an understanding with Britain and France appear to be the greater, but nothing can be prognosticated with certainty. It also remains a question of the future whether, and to what extent, such a rapprochement would affect German commercial relationships with Spain.

In Italy the state of affairs during the past year has been the reverse of satisfactory, although our own relations with this market have been very animated and have developed in a pleasant manner. The effects of the costly and unexpectedly long drawn-out war in Tripoli have manifested themselves in the form of a pronounced attitude of reserve in capitalistic circles; and among other factors which have unfavourably affected commerce and industry were failures in the cotton trade, a serious handicapping
of the silk industry in the markets of the world by Japanese competition, and the poor corn- and oil-harvests. It is only since the war has been brought to a close that business-confidence has begun to revive, and we have no doubt that henceforth the country will steadily progress towards a complete restoration of healthy commercial conditions.

In Switzerland and Holland business has been normal and no events calling for special notice have occurred. The favourable situation of the Dutch colonial market has not been without its effect upon the economic development of the Mother-country.

The commercial condition of Russia has given little cause for congratulation. The official statistics for the year 1912 show that the foreign trade of this country, which is such an important market for our manufactures, has by no means equalled the expectations which might justifiably have been entertained in view of the actual developments of the past few years. Both the imports and the exports of Russia have suffered a not inconsiderable decline in the year 1912 as compared with the previous year, and unless the export-trade revives we shall be compelled to take a not very favourable view of the probable increase in the purchasing power of the Russian nation within the immediate future. Suspensions of payment have increased at a truly alarming rate during the year 1912, and the most recent reports give no indication of any improvement in the situation. Caution in the granting of credit has been more necessary than ever before, even at the risk of an occasional loosening of the commercial bonds between ourselves and our Eastern neighbour. Fortunately, those branches of industry in which our products are consumed have escaped without serious losses, and if it were not that unfavourable reports of the situation are coming to hand from all quarters, we should not be at all disposed, in the light of our own experience, to take a pessimistic view. It is obvious, however, that the Russian military preparations on the Western and Southern frontiers of the Empire were bound to provoke a certain nervous tension in all departments of commerce, and in the interest of all parties concerned it is a matter for rejoicing that on the initiative of Austria the troops in the frontier-districts have in the meantime been demobilised.

Among the Balkan States business with Roumania alone has afforded occasion for a certain degree of satisfaction, although in this country, too, coming events cast their shadows before, and the war in which the neighbouring States were involved inflicted severe injury upon trade and industry. Bulgaria, Servia, Greece and that distressful country, Turkey, have been more or less blotted out from the list of selling-markets since the beginning of the war, and from the moment when the moratoria (the official suspensions of cash-payments), were proclaimed, commercial intercourse with them has been almost entirely at a standstill. How long it will take after the conclusion of peace before the nations concerned in the struggle have sufficiently recovered from their grave financial sacrifices to make it possible to speak again of regular commercial intercourse, and whether, in fact, Turkey will ever surmount the consequences of her defeat, are problems which must be allowed to repose in the lap of the future.

The remaining European consuming markets offer no occasion for remark; we will only place on record the fact that during the past year the Scandinavian Kingdoms, in so far as they make use of our products in their industries, have been extremely good buyers, and that our turnover with these countries has shown a normal growth.

According to reports from the German Consulate at Alexandria, the economic condition of Egypt in the year 1912 has been satisfactory, the cotton-crop having yielded a good result. During the closing months of the year, however, the Balkan war and the uncertainty of the political situation in Europe have had an unfavour-
able effect, inasmuch as these events have caused the banks to restrict credits, whereby the import-trade in particular has been restrained. Hence, as compared with the year 1911 (when, however, the figures were the highest ever reached), the value of the imports has fallen by 5 p.c. In the country-districts debts were paid with fair punctuality, but in the towns their collection was often attended with difficulties. The collections on behalf of the wounded in the Turkish army have adversely affected the receipt of accounts due, about 250000 £E, or rather more than a quarter of a million Sterling having been sent out of the country as a result of these collections. With the exception of one banking firm in Alexandria, none of the larger foreign concerns have suspended payment, but there have been numerous failures among the native traders. It is expected that when peace is restored there will be a great revival of business, especially in view of the fact that last year's cotton crop amounted to at least 350000 tons and that the price of cotton has remained normal. According to official statistics of the trade of Egypt, the total imports in the year 1912 reached a figure of 25907759 £E, as compared with 27227118 £E in the year 1911; a decrease of 1319359 £E. The total exports in the year 1912 reached a value of 34574321 £E, whereas the total for the year 1911 was 28598991 £E, which shows an increase in this department of 5975330 £E.

The imports into Egypt from all countries with the exception of the British possessions in Eastern Asia, the United States, Belgium, Greece, Holland, Sweden and Norway, show a decrease for 1912 as compared with the previous year. British imports have fallen off in value by 8 p.c., Austrian by 18 p.c. (especially in cottons, woollens, and metal goods), but the imports of British flour and of Austrian sugar show an increase. The imports from France have decreased by 13 p.c., chiefly in flour, cottons and woollens, and metal goods; those from Italy by 15 p.c., also chiefly in flour, cottons and woollens, but cotton-yarn from this country shows an increase. Imports from Turkey show a reduction of only 2 p.c., mostly in corn, coffee, wood, charcoal and textiles, but there was an increase in the imports of living animals, wine, oil and soap. Shipments from Russia have suffered a decline of about 11 p.c., chiefly in sugar, but the imports of Russian petroleum have increased. The imports from Belgium have fallen by 4 1/2 p.c. The imports into Egypt from Germany were less by 79565 £E, or 5 p.c. than in 1911. Here it is principally the trade in coal, stoneware, china and glassware, cottons and woollens that has decreased, whereas there has been a considerable increase in the imports of metal goods.

Our own experience in our relations with our Egyptian customers differs from the particulars given above in this respect, that we have not suffered any reduction in our turnover as compared with 1911.

Our New York branch again gives an extraordinarily favourable account of the commercial position in the United States of North America. The result of the Presidential Election has generally been accepted as the best solution of the somewhat tangled conditions of the hotly-fought three-cornered political struggle. The general expectation is that President Wilson and his democratic legislature will not show a tendency to extremes in their dispositions, and commercial circles have therefore hardly shown any such signs of nervousness as have usually attended the change of the administrative power from one political party to the other, in the past.

All the preliminary work connected with the proposed Tariff revision has practically been finished under the old administration, and it is generally believed that the new House will adopt the schedule of the Underwood Tariff with the comparatively slight modifications which may result from the hearings held in January before the
Value of imports and exports of Essential Oils from and into the United States, in the second half of the years 1912 and 1911 respectively.

<table>
<thead>
<tr>
<th>Month</th>
<th>Imports</th>
<th>1912</th>
<th>1911</th>
<th>Exports</th>
<th>1912</th>
<th>1911</th>
</tr>
</thead>
<tbody>
<tr>
<td>July</td>
<td>duty-free</td>
<td>$104,415</td>
<td>$176,229</td>
<td>Peppermint Oil</td>
<td>$28,793</td>
<td>$9,190</td>
</tr>
<tr>
<td></td>
<td>dutiable</td>
<td>49,926</td>
<td>66,848</td>
<td>Other indigenous Oils</td>
<td>24,282</td>
<td>32,323</td>
</tr>
<tr>
<td>August</td>
<td>duty-free</td>
<td>292,200</td>
<td>196,190</td>
<td>Foreign Oils, duty-free</td>
<td>6,115</td>
<td>3,709</td>
</tr>
<tr>
<td></td>
<td>dutiable</td>
<td>92,802</td>
<td>53,467</td>
<td>&quot; dutiable</td>
<td>1,567</td>
<td>7,746</td>
</tr>
<tr>
<td>September</td>
<td>duty-free</td>
<td>281,895</td>
<td>139,037</td>
<td>Peppermint Oil</td>
<td>12,605</td>
<td>25,864</td>
</tr>
<tr>
<td></td>
<td>dutiable</td>
<td>84,595</td>
<td>56,127</td>
<td>Other indigenous Oils</td>
<td>26,587</td>
<td>24,636</td>
</tr>
<tr>
<td>October</td>
<td>duty-free</td>
<td>357,216</td>
<td>164,169</td>
<td>Foreign Oils, duty-free</td>
<td>3,179</td>
<td>1,021</td>
</tr>
<tr>
<td></td>
<td>dutiable</td>
<td>81,331</td>
<td>73,224</td>
<td>&quot; dutiable</td>
<td>3,222</td>
<td>5,711</td>
</tr>
<tr>
<td>November</td>
<td>duty-free</td>
<td>150,497</td>
<td>180,190</td>
<td>Peppermint Oil</td>
<td>27,271</td>
<td>74,193</td>
</tr>
<tr>
<td></td>
<td>dutiable</td>
<td>106,356</td>
<td>61,707</td>
<td>Other indigenous Oils</td>
<td>18,355</td>
<td>27,083</td>
</tr>
<tr>
<td>December</td>
<td>duty-free</td>
<td>262,914</td>
<td>199,591</td>
<td>Foreign Oils, duty-free</td>
<td>2,824</td>
<td>1,815</td>
</tr>
<tr>
<td></td>
<td>dutiable</td>
<td>101,667</td>
<td>73,924</td>
<td>&quot; dutiable</td>
<td>7,520</td>
<td>4,800</td>
</tr>
</tbody>
</table>

Total value of imports for the 2nd half-year 1912 $1,965,814
" " " " " " whole year 1912 $4,116,641
" " " " " " 1911 1,440,703
" " " " " " 1911 2,875,442

Total value of exports for the 2nd half-year 1912 $509,276
" " " " " " whole year 1912 $850,923
" " " " " " 1911 485,050
" " " " " " 1911 798,484

Committee of Ways and Means. This belief is strongly supported by the fact that the new House will be of the same political complexion as the old, and that the new Democratic Senate is not likely to oppose the administrative policy.

It is a fact that the Tariff changes proposed for the Chemical Schedule are by no means immaterial, and determined efforts have been made by the authoritative representatives of the various branches of our trade to have objectionable measures set aside. The Manufacturing Perfumers' Association, the Flavoring Extract Manufacturers' Association, as also the National Conference of Soap Manufacturers presented their arguments in the most skilful manner in behalf of their constituents, but it has been stated upon good authority that the legislative bodies will hardly change their views, which culminate in the presumption that the great majority of manufactured articles in which essential oils are used belong to the class of luxuries and can therefore bear an additional burden for the sake of revenue. Regrettable as is this...
view, we hope that the American trading and manufacturing circles, which have solved harder problems in the past, will find ways and means to overcome the impending difficulties and to adjust themselves to the given conditions.

The cardinal points of the proposed Tariff-changes affecting our trade are the following:—

All essential oils and other odoriferous materials which have been on the free list of the Payne-Aldrich Tariff are scheduled to pay a duty of twenty p. c. ad valorem under the new Underwood Tariff. As a kind of an equivalent for this rather radical imposition, the new Tariff provides that all those essential oils which have paid a duty of twenty-five p. c. ad valorem heretofore, shall also be taxed at the rate of twenty p. c. ad valorem in future. Other special provisions in the Tariff of interest to our trade are the following specific stipulations: Duty on oil of peppermint 25 cents p. lb.; on menthol 50 cents p. lb. and on vanillin 10 cents p. oz. As President Wilson will most probably call an extra session of Congress for April 1, we shall soon be in a position to know definitely with which changes in Tariff matters we will have to count in future.

Contrary to the general expectation that the Acting Chief of the Bureau of Chemistry, Dr. R. E. Doolittle, would be definitely installed in this important office, or, in the alternative, that the selection of a successor to Dr. Harvey W. Wiley would be left to the new administration, Dr. Charles Alsberg, formerly connected with the Bureau of Plant Industry of the U. S. Department of Agriculture, has been appointed Chief of the Bureau of Chemistry on December 17th, 1912. Whether he will be retained by the new administration, or whether, with a new Secretary of the Department of Agriculture, another change in this office will be made, is mere conjecture at the present moment. One fact, however, has been established in the meantime in reference to Dr. Alsberg, namely that his views, at least in reference to the patent medicine situation in the United States, are sound and decisive, as expressed by him in a recent speech made before a meeting of the National Association of Manufacturers of Medicinal Products of the United States.

Our business during the year 1912 has been very satisfactory, as already stated in our last Report; a fact which is the more remarkable because other presidential years have almost invariably produced at least a certain stagnation in business matters. If any apprehensions exist in regard to the effect which the change in the Administration from a Republican to a Democratic régime and the Tariff revision may have on the development of trade, we have, at least, not noticed them in our particular branch. The early contracting during the year 1913 has been as satisfactory as ever, and the months so far elapsed in this year show handsome increases over their respective predecessors in 1912. Everything, therefore, points again to a successful and prosperous development of business in the year 1913, as we do not believe that international complications are likely to affect business in the United States.

The value of the exports of essential oils to the United States from the Consular district of Leipzig, in which our firm plays the leading part, have been as follows:—

<table>
<thead>
<tr>
<th>Year</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>$363046.</td>
</tr>
<tr>
<td>1911</td>
<td>$289368.</td>
</tr>
<tr>
<td>1910</td>
<td>$215011.</td>
</tr>
</tbody>
</table>

Our business in the Dominion of Canada is also showing a healthy and steady increase and promises, with the rapid general development in this particular country, to grow in time to very respectable dimensions.
Throughout the past half-year, trade in Cuba, owing to the impending Presidential Election and its attendant political turmoil, has been exceedingly sluggish. To the political excitement must be added the fact that the liqueur-manufacturers have had fresh difficulties placed in their way by the enormous increase in the amount of cash-security which must be lodged with the authorities who control the traffic in alcohol. Now that President Gomez with his ruinous administration has gone into retirement, high hopes are centred upon his successor, General Menocal, who enjoys an excellent reputation. Unless these hopes should be disappointed, we may look forward to a considerable improvement in business, for the sugar-crop will again be enormously large; in fact, it is asserted that it will be the largest ever produced in the island. The estimate is 1200000 tons.

Mexico, an important consuming market, is notoriously passing through a crisis of the most serious kind which can possibly befall a country. The hideous struggles in the streets of the beautiful capital, costing as they did not only many human lives but also causing enormous material waste, have filled the entire civilised world with disgust, which was deepened by the murder of ex-President Madero with several of his closest relatives and associates. It must be said, however, that some of the latter were highly unpopular. It is still extremely doubtful whether the new régime will be able to re-establish peace in the country, and to regain the confidence of financial circles. The future of Mexico, a country which was so flourishing and so rapidly developing in the days of old Porfirio Diaz, and which then enjoyed general confidence, is now exceedingly uncertain, and until the present Government has given evidence of its ability to hold its own, foreign capital will assuredly maintain a most reserved attitude.

Once more we can only speak favourably with regard to our trade with Brazil. It is true that the Brazilian soap- and perfume-industry is stated to be still in a backward stage of development, inasmuch as at the present time it is only capable of producing goods of ordinary quality, but we are nevertheless able to record with satisfaction that the sale of these oils and aromatic substances of which the use is restricted to the preparation of really good and of the finest perfumes, is likewise rapidly on the increase. In Brazil, in common with all tropical countries, strong perfumes are everywhere the most popular, and the requirements of the Republic of goods in our branch are therefore very considerable. This notwithstanding, however, the country will always remain a good customer for European scents in the put-up form, of which France is the principal supplier. The United States, Spain, Germany, Belgium, England, and Switzerland are also, however, participating in the imports.

The general industrial advance of Brazil is shown in the fact that, according to the latest statistics, the country already possesses 3254 factories and industrial undertakings, employing an aggregate of 151841 hands. The capital invested in these undertakings amounts to 665676000 milreis, that is to say to approximately 40 millions Sterling ($ 200 million). Rio de Janeiro, the capital, has 670 factories, representing a capital of 169989000 milreis and an annual output of the value of 232028000 milreis. The second place is taken by the city of São Paulo, with 326 factories, representing a capital of 128702000 milreis and an output of 118087000 milreis. Rio Grande do Sul occupies the third place. The most important industry is that of textiles, which alone numbers 194 factories with a capital of 268170000 milreis. The principal products of this industry are coffee-bags and cotton-goods.

That the future of Brazil is regarded in the most hopeful manner abroad is clearly shown by the fact that the capital of foreign companies operating within the country
has increased in the years 1910 to 1911 by about 325 p.c. and at the close of 1911 represented the imposing total of £20,767,860. This is surely the best evidence of the confidence which is felt in the development of this country of enormous natural riches.

The favourable economic condition of the Argentine Republic throughout the past year has naturally contributed to an extremely brisk demand for our manufactures, the sale of which is chiefly determined by the demand for luxuries. Hence the value of our exports to this market, where competition is very keen, has risen considerably. We expressly lay stress upon this fact, because the trade-statistics for 1912 show a falling-off in the total value of all German exports to Argentina of about 2 million Pesos gold. Germany, it is true, still occupies, after the United Kingdom, the principal place among the countries that supply the Argentine, but unless ways and means are found to arrest the retrogression in German exports to this market, the United States will soon dispute Germany her position among the importing countries. We are unable to form an opinion of the causes of the decline. The total value of the imports into and exports from Argentina in 1912 reached $865,244,725 gold, exceeding that of 1911 by $173,736,501 gold, equal to over 25 p.c.

The rapid and steady increase of the foreign trade of Argentina is clearly shown in the subjoined table giving the value of the imports and exports during the last decade.

<table>
<thead>
<tr>
<th>Year</th>
<th>Imports $ Gold</th>
<th>Exports $ Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>1903</td>
<td>131,206,600</td>
<td>220,984,524</td>
</tr>
<tr>
<td>1904</td>
<td>187,305,969</td>
<td>264,157,525</td>
</tr>
<tr>
<td>1905</td>
<td>205,154,420</td>
<td>322,843,841</td>
</tr>
<tr>
<td>1906</td>
<td>269,970,521</td>
<td>292,253,829</td>
</tr>
<tr>
<td>1907</td>
<td>285,860,683</td>
<td>296,204,369</td>
</tr>
<tr>
<td>1908</td>
<td>272,972,830</td>
<td>366,005,341</td>
</tr>
<tr>
<td>1909</td>
<td>302,756,095</td>
<td>397,350,528</td>
</tr>
<tr>
<td>1910</td>
<td>351,770,656</td>
<td>372,626,055</td>
</tr>
<tr>
<td>1911</td>
<td>366,810,686</td>
<td>324,697,538</td>
</tr>
<tr>
<td>1912</td>
<td>384,853,469</td>
<td>480,391,256</td>
</tr>
</tbody>
</table>

In February of this year the promulgation of a new law imposing taxation upon put-up medicinal preparations and upon perfumes provoked a protest by the pharmacists and druggists of Buenos Aires. This movement of protest culminated into something like a strike, about 400 out of a total of 420 shops being closed down by the proprietors after the Government had declined to listen to their representations. The Government thereupon took steps to organise the sale of remedies through the Department of Public Health and began to consider coercive measures against the pharmacists on strike, but in the end the authorities were compelled to give way, and to announce that the coming into force of the law would be postponed for the time being. The law compels the importer to pay a tax upon every one of his innumerable medicinal preparations and perfumes according to their price to the public. The tax therefore varies, and is determined by the retail selling price. Every business man will agree that in view of the many thousand of trifling commodities affected, such a scheme is impossible of execution. One retail tradesman sells a given article at a certain price, another tradesman sells the same article at a different price, according to his dead charges or the character of his customers. Therefore the scheme would be a permanent source of claims and penalties, even if the importers were acting
in good faith according to the best of their knowledge. But even an attempt to act in this manner is impossible, because there is no basis whatever to proceed upon. The businesses affected do not object to an increased taxation of perfumes, but they ask that this shall be levied as part of the customs duty, and they refuse to submit to the chicanery of a complicated system of Inland Revenue stamps.

It is to be hoped that in future our clientele will not be vexed by troubles of this kind, which inflict serious economic injury upon them.

In Uruguay also the situation during the past year has been satisfactory, the wool-clip having yielded a better result than in 1911, because the climatic conditions had been favourable to the sheep. The high wool-prices realised in Europe left plenty of profit and therefore stimulated the purchasing power of the population.

With regard to the sale of perfumery, soaps and toilet-preparations in Uruguay, the German Consulate at Montevideo reports that the lion's share of the imports, over 70 p. c., falls to France. Next in order come England, Germany, the United States of America, and Belgium. The subjoined figures show that during the past ten years the imports from Germany have not only increased actually, but also relatively to the total imports.

<table>
<thead>
<tr>
<th>Year</th>
<th>Total Imports</th>
<th>Imports from Germany</th>
<th>Proportion of total Imports</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pesos</td>
<td>Pesos</td>
<td>p. c.</td>
</tr>
<tr>
<td>1902</td>
<td>74 037</td>
<td>4 157</td>
<td>5.61</td>
</tr>
<tr>
<td>1903</td>
<td>76 110</td>
<td>4 616</td>
<td>6.06</td>
</tr>
<tr>
<td>1904</td>
<td>50 110</td>
<td>2 471</td>
<td>4.93</td>
</tr>
<tr>
<td>1905</td>
<td>98 568</td>
<td>5 698</td>
<td>5.77</td>
</tr>
<tr>
<td>1906</td>
<td>109 103</td>
<td>5 435</td>
<td>4.88</td>
</tr>
<tr>
<td>1907</td>
<td>155 901</td>
<td>6 130</td>
<td>3.96</td>
</tr>
<tr>
<td>1908</td>
<td>137 988</td>
<td>8 299</td>
<td>6.01</td>
</tr>
<tr>
<td>1909</td>
<td>138 556</td>
<td>9 078</td>
<td>6.55</td>
</tr>
<tr>
<td>1910</td>
<td>127 242</td>
<td>10 785</td>
<td>8.47</td>
</tr>
<tr>
<td>1911</td>
<td>148 642</td>
<td>13 197</td>
<td>8.87</td>
</tr>
<tr>
<td>10 Years</td>
<td>1 116 257</td>
<td>69 866</td>
<td>6.25</td>
</tr>
</tbody>
</table>

According to the German official statistics, the imports into Uruguay of soap, in the solid and liquid form, were as follows:—

1910 . . . . . . . . 17 400 Kilos, value 29 000 Marks
1911 . . . . . . . . 19 100 " " 35 000 "

In Uruguay itself there are several large soap works, which produce chiefly common grades, but in part also household soaps of better quality at low prices. The raw material for the manufacture of soap is obtainable cheaply in the country itself.

We are also able to report favourably again on business in Chile. The principal products of this country, copper, nitrate of soda and agricultural produce, have been exported in increased quantities and have brought satisfactory prices. The resultant profits will stimulate the consumption of foreign, including German, manufactures on a still more extensive scale than at present, as soon as the excessive stocks now held in the country have been used up. The existence of these stocks has already brought about the ruin of many business firms. According to a report by the German Consul-General at Valparaiso the crop-prospects for 1912/13 are good; cattle-raising also has made good progress, which fact is the more important because the prices
of live stock have risen appreciably. We are therefore justified in cherishing the best hopes of the further expansion of German business-relationships with this consuming market.

There is but little ground for satisfaction with the state of affairs in Peru. The Deutsche Überseeische Bank, in its commercial report for 1912, states that no improvement was noticeable last year in the economic conditions of the country, although the Presidential change in September last took place very quietly. Of course, during the brief period of its existence, the new Government has not yet been able to take all the measures necessary for placing the national finances on a sound footing, but certain economies have already been introduced into the Budget which it is hoped will lead to the future establishment of a better equilibrium between revenue and expenditure. The issue of a foreign loan, which appears to be necessary in order to pay off old debts and to provide for the deficits of previous years, as well as for the execution of certain financial schemes, is planned for the current year. Continued consideration is being given to railway-projects; it would appear that the prospects of the construction of the railway to the river Ucayali, which is to connect the capital with the eastern provinces of Loreto and Iquitos, are now more likely of realisation; at any rate it is stated that the necessary money has been found. Congress has already sanctioned a grandiose scheme for the irrigation and colonisation of the arid coast-strip, and it is reported that American capitalists are interesting themselves in this plan. It deserves to be recorded as a special merit of the new Government that it has set on foot negotiations with the neighbouring Republic of Chile which warrant the hope that the question of Arica and Tacna, so long outstanding between the two countries, is at last on the road to settlement; so much at any rate appears certain that both governments are animated by a genuine desire to remove this ancient cause of dissension. The high prices of copper and silver have assisted in reviving the mining-industry. Agriculture also has undergone a marked development, notwithstanding that the prices of the principal articles of export from Peru, such as sugar, cotton, and rice, have been lower than in the previous year.

For all these reasons an early improvement in the condition of the country is to be expected, provided that the new Government shows itself able to cope with the requirements of the situation. But it would not be wise to build too high anticipations upon the future of the German export-trade to Peru, inasmuch as the population of the country will probably always remain lacking in genuine purchasing-power, unless, indeed, the opening of the Panama Canal should bring about an increase in this respect.

We are once more in a position to give a favourable account of trade with Japan; the second half of the year 1912 in particular has seen an appreciable growth in our exports to this important market. The heavy importations of commodities of our branch of manufacture, which came into the country just prior to the increase in the Customs Tariff in July 1911, have in the meantime been consumed, and the more settled state of things in China has not been without a favourable influence upon the export-trade in Japanese soaps and perfumery.

Generally speaking the high prices of many of our principal oils have somewhat impeded their sale in Japan, but we have found some compensation in the increased interest which has been manifested in the excellent substitutes with the introduction of which we have specially occupied ourselves last year.

The total value of Japanese imports in 1912 was 618,972,578 yen (513,805,705 yen in 1911), and of exports 526,980,842 yen (447,433,888 yen in 1911). The imports have
therefore surpassed the exports by nearly 92 million yen, as compared with 66 million in the previous year.

In spite of this considerable progress in commercial intercourse with foreign countries a few factors were observable which were unfavourable to development. For although the last rice-crop was a fair average one, speculators had succeeded in driving up prices to an unexampled level, and in maintaining them there for quite a considerable time. This circumstance naturally depressed seriously the whole economic life of the nation, because wages and costs of maintenance depend directly upon the price of this staple foodstuff, and the higher selling prices do not benefit the people at large, but flow mainly into the pockets of a group of speculators and capitalists. Another impediment in the way of the development of trade was the vacillating policy of the Government. Since the late Emperor's death the Government no longer exercised absolute control over the people and Parliament, and serious conflicts ensued in which even the powerful Minister, Count Katsura, was overthrown. It remains an open question whether the new Cabinet will be able to realise the long-cherished hope of a reduction of taxation, but the threatening attitude of the people has certainly brought the probability of such an eventuality very much nearer.

Trade between Japan and China has been very brisk. But the excess of Japan's exports to China over her imports from that country has been greater last year by two million yen than in 1911; the imports having fallen off by 60,000 yen, evidently owing to the general stagnation of shipments from China. As soon as the situation in China (a country which forms such an important outlet for Japanese products) has become sound again, the Japanese export trade will no doubt commence to progress once more.

The ceaseless activity of the Japanese spirit of enterprise is evidenced by the fact that according to official returns1) 3888 new trading companies were founded in that country last year with a total paid-up capital of 110,919,882 yen. According to the Bank of Japan, the total amount of capital subscribed for new undertakings or towards the increased capitalisation of existing concerns, was 521 million yen, divided as follows:—

<table>
<thead>
<tr>
<th>New</th>
<th>Already in existence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banks</td>
<td>13,900,000</td>
</tr>
<tr>
<td>Spinning Mills</td>
<td>12,900,000</td>
</tr>
<tr>
<td>Electrical industries</td>
<td>12,170,000</td>
</tr>
<tr>
<td>Mines</td>
<td>9,020,000</td>
</tr>
<tr>
<td>Marine products</td>
<td>8,050,000</td>
</tr>
<tr>
<td>Railways and Tramways</td>
<td>32,315,000</td>
</tr>
<tr>
<td>Manufacturing industries</td>
<td>118,195,000</td>
</tr>
<tr>
<td>Steamships</td>
<td>2,300,000</td>
</tr>
<tr>
<td>Insurance</td>
<td>1,000,000</td>
</tr>
<tr>
<td>Commerce and other pursuits</td>
<td>123,636,000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>333,486,000</strong></td>
</tr>
</tbody>
</table>

The condition of affairs in China continues to be very uninviting and some time must still elapse before the sequelae of the revolution have been surmounted, and before the new form of government has gained the confidence of the people in such a measure that it is possible to expect a real amelioration in trade and traffic.

1) Handelsmuseum XXVIII, 13.
According to a French Consular Report reproduced in the Deutsche Export-Revue the following toilet-soaps are most in demand among the Chinese in the port of Swatow (Southern China): a French brand selling at 0,20 dollars; a German glycerin-soap selling at 0,40 dollars the piece; "Magical soap", an English brand, at 0,10 dollars per box of two pieces; and a Japanese brand called "Pet Dog" at 0,15 dollars the piece. The use of laundry-soaps is increasing. The most popular English laundry-soap costs 4,50 dollars per box of 20 bars, or 50 lbs. The price of a bar of this soap is 0,30 dollars. Some time ago the Compagnie Sino-française at Swatow made a successful attempt to introduce Marseilles soaps. Other saleable toilet-articles are: New York vaseline-pomade at 0,10 dollars per pot of 3 oz.; Japanese combs at 0,15 dollars, and British and German combs at 0,30 dollars each; British shaving basins at 0,30 dollars each, and British shaving-basins made of aluminium at 0,90 dollars. The dollar above referred to is the Mexican Dollar of 24,438 g. fine silver, compared with the Haikwan Tael of 38,346 g. European perfumery is scarcely able to maintain competition with the extremely low-priced Chinese and Japanese articles. In the year 1910 the value of the imports of perfumery was 8263 H. Taels; in 1911, when trade was somewhat disturbed owing to the political unrest, it was only 5456 H. Taels.

The total value of China's perfumery imports in 1910 was 29,443 Haikwan Taels. In 1911 it rose to 34,006 H. Taels. For 1912 no statistics are yet available.

Before proceeding, as usual, to the consideration in detail of our various manufactures, we venture to express the hope that our Report in its new size (8½ x 6½ in., being No. IX of Ostwald's Universal or "Welt-Format", 16 x 22,6 cm) will continue to enlist the interest of its readers.

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Commercial Notes and Scientific Information on Essential Oils.

Almond Oil, Bitter. The nitrile glucosides which occur in nature have hitherto been described comprehensively as amygdalin; the possibility that, in addition to the ordinary amygdalin, isomerides or stereomerides, as for example iso-amylgladin or neo-amygdalin 1) might occur, having simply been disregarded. In order to clear up this matter, L. Rosenthaler 2) has prepared the glucosides of the seeds of apricots, peaches, plums, apples, and quinces and ascertained the following constants of each of these bodies: melting point, specific rotation, molecular weight, nitrogen-content and optical rotation of the mandelic acid obtained by the saponification of the glucosides. The result of his investigations showed that all the data agreed with those for amygdalin and that therefore the glucoside contained in the seeds referred to is identical with the amygdalin of bitter almonds.

With the object of isolating the glucosides, Rosenthaler has boiled the seeds, after freeing them from fat, with alcohol. He has further tested the seeds containing amygdalin for the presence of glucosides of the type of mandelonitrile glucoside. For this purpose he regards Bourquelot's method, in which any saccharose which may be present is decomposed with invertin, as unsuitable, because, in his view, invertin not only decomposes the cane-sugar, but also the amygdalin.

1) Comp. Report October 1907, 13; Report October 1909, 19. 2) Arch. der Pharm. 250 (1912), 298.
Here Rosenthaler is mistaken, as Bourquelot and Hérissey\(^1\) have shown in their rejoinder to his statements. For amygdalin is not affected by invertin at all, but it is affected by amygdalase, a ferment which differs from invertin.

It is true that Rosenthaler's dictum was based upon experiments; but, as Bourquelot and Hérissey assume, he has, without questioning, employed yeast which contained both invertin and amygdalase, as is often the case. For this reason it is necessary in biological experiments such as carried out by Rosenthaler, first to test the yeast for the presence of amygdalase. We cannot spare the space here to enter into details of the interesting experiments which the authors have carried out with various preparations of invertin and with amygdalin. It was clearly shown, however, that pure invertin is incapable of splitting-up amygdalin.

A paper by Rosenthaler\(^3\) on the distribution of emulsin-like enzymes was published afterwards. The older statements with regard to the distribution of emulsin exclusively refer to that constituent which sets free hydrocyanic acid and benzaldehyde from amygdalin. But according to more recent views, emulsin is a mixture of various enzymes which differ in their action and to which different names have been given. Amygdalin is first split up by amygdalase into glucose and mandelonitrile glucosides. The latter is decomposed by prunase\(^4\), a \(\beta\)-glucosidase, into glucose and benzaldehyde cyanohydrin; while the benzaldehyde cyanohydrin, in its turn, is split up by an oxy-nitrilase into benzaldehyde and hydrocyanic acid. The synthesis of optically active nitriles is effected by an oxynitrilase, as Rosenthaler intends henceforth to call the enzyme which he has previously designated by the name of \(\delta\)-emulsin\(^5\).

Rosenthaler has prepared enzyme-preparations from numerous plants and parts of plants, and has examined them with a view of ascertaining whether they develop similar action as does the almond-emulsin; that is to say whether they decompose amygdalin until hydrocyanic acid appears in the distillate, and whether in synthetical experiments and in the splitting-off of nitrile they yield optically active nitriles\(^6\).

The results obtained by Rosenthaler are as follow:

1. Amygdalin is decomposed by preparations from the following material:

- Barks: *Prunus Padus*, L.
- Subterranean organs: *Sambucus Ebulus*, L.
- Spores: *Linum usitatissimum*, L.
- Sclerotium: *Secale cornutum*.

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Decomposition of amygdalin did not occur in the preparations but in the material itself with:

Fruits: *Pimpinella Anisum*, L., *Coriandrum sativum*, L.
Flowers: *Lamium album*, L.
Fruit bodies: *Polyporus sulphureus*, Fries.

2. The synthetic experiment gave a positive result with preparations from the following material:

Fruits: *Coriandrum sativum*, L., *Sorbus Aucuparia*, L.
Stigmata: *Zea Mays*, L.
Subterranean organs: *Sambucus Ebulus*, L.

3. Decomposition of nitrile gave a positive result with preparations of the following material:

Seeds: *Pangium edule*, Reinw., *Hydnocarpus Wightiana*, Bl. with all the *Pomaceae* and *Prunaceae* quoted under 2.

It is remarkable that the leaves of *Taraktogenos Blumei* contain an enzyme which in the synthetic experiment does not afford d-benzaldehyde cyanohydrin, as do the enzymes of the *Prunaceae*, but the l-modification, and which may therefore be designated as l-oxyanitirile.

In the preparation of emulsin from plant material the behaviour towards alcohol of different degrees of concentration must be taken into account, and in this matter E. Bourquelot and M. Bridel have made interesting experiments. They have found that in warming with dilute alcohol (50 to 80 p. c.) the emulsin loses its activity at a much lower temperature than is the case in heating with concentrated spirit. After boiling emulsin for 2 minutes with absolute alcohol, none of its activity had been lost. In order to kill the ferments which are contained in the plants it is therefore advisable not to use absolute alcohol, but alcohol of about 60 p. c. This concentration is obtained by dipping green parts of plants in boiling 95 p. c. alcohol, or by treating dry plant-

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1) *Journ. de Pharm. et Chim.* VII. 7 (1913), 27, 65.
material, or fruit and seeds with alcohol of about 80 p. c. In this treatment the water which is present in the cells dilutes the spirit to the desired strength.

Rosenthaler has made experiments in decomposition with several of these emulsin-preparations, but it would lead us too far describe them in detail.

In conclusion, Rosenthaler gives an arrangement to indicate the processes which take place in the amygdalin-emulsin system. This arrangement we reproduce textually below:—

I. Amygdalin, by the action of amygdalase, affords mandelonitrile glucoside and glucose.

II. Mandelonitrile glucoside is resolved by the action of prunase into $d$-benzaldehyde cyanohydrin and glucose.

III. $d$-benzaldehyde cyanohydrin is resolved by $d$-oxynitrilase into benzaldehyde and hydrocyanic acid.

IV. Benzaldehyde and hydrocyanic acid unite under the influence of a $d$-oxynitrilese to form $d$-benzaldehydecyanohydrin.

V. In addition, benzaldehyde and hydrocyanic acid afford inactive benzaldehyde cyanohydrin.

VI. Inactive benzaldehyde cyanohydrin is capable of being split up asymmetrically by $d$-oxynitrilase, giving rise to $l$-benzaldehyde cyanohydrin. But in emulsin-preparations which are rich in this enzyme it is possible that, as a result, the benzaldehyde cyanohydrin which is formed in the process of the decomposition of amygdalin may be lævorotatory.

It will remembered that at the time we referred to an interesting asymmetric synthesis of $d$-benzaldehyde cyanohydrin which had been carried out by L. Rosenthaler from benzaldehyde and hydrocyanic acid by the action of emulsin. G. Bredig and P. S. Fiske have now discovered that when an optically active alkaloid is used as a catalyser the generation of benzaldehyde cyanohydrin from its components, hydrocyanic acid and benzaldehyde, takes an optical-asymmetric course, that is to say, that asymmetric synthesis can be achieved by a catalyser of known constitution exactly in the same manner as by an enzyme. Bredig and Fiske employed quinine and quinidine as catalysers. With quinine, a dextrorotatory cyanohydrin was obtained, which under saponification gave rise to $l$-mandelic acid, while with quinidine, an isomeride of quinine, lævorotatory cyanohydrin and dextrorotatory acid were obtained. In equivalents (molecules) the quantity of the optically active mandelic acid which is obtained is greater than that of the alkaloid which has been used as a catalyser, hence the character of the reaction as a catalysis is assured. The authors mention the curious fact that the cyanohydrins possess a remarkably strong affinity with alkaloids such as quinine, quinidine, &c. This is the reason why, in certain circumstances, it is exceedingly difficult to remove the latter from anhydrous cyanohydrin solutions by shaking out with aqueous hydrochloric acid and why, on the other hand, a non aqueous benzaldehyde cyanohydrin solution is capable of completely abstracting the alkaloid from an aqueous hydrochloric acid solution by shaking-out.

F. D. Dodge, who has taken up the estimation by titration of benzaldehyde (also see p. 124), has given some particulars of his investigations at the Eighth International

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Congress of applied Chemistry which assembled in September 1912 at Washington. Dodge has made control-tests of some of the methods which have been recommended for this estimation and has found that Sadler's method, which has been incorporated in the Pharmacopeia of the U. S. does not give satisfactory results. The method devised by Ripper gave better values, although these, too, are only approximately accurate. Ripper shakes up the aldehyde with a bisulphite-solution of known strength and titrates back the excess of bisulphite with iodine solution at a low temperature. According to Dodge, the most suitable manner of carrying out this method is as follows: 0.15 g. aldehyde or bitter almond oil is weighed in a flask containing exactly 25 cc. of a, say, 1/5 n. bisulphite solution, and brought to solution by gentle shaking. The flask is then closed, left standing in ice-water for 1½ to 2 hours, after which the ice-cold solution is titrated with decinormal iodine-solution, starch being used as an indicator. A blank test is carried out in the same way, the benzaldehyde content being calculated from the difference (1 cc. decinormal iodine solution = 0.0053 g. benzaldehyde). The reaction is completed as soon as the blue colour persists for a few seconds. By this method Dodge, in the case of pure benzaldehydes, found from 94.8 to 99.0 p. c.

Determination with hydroxylamine (according to Walther, as modified by A. H. Bennett, comp. Reports April 1909, 110 and October 1909, 153) offered no advantages as compared with the iodometric process, inasmuch as in the case of pure benzaldehydes only 93.5 and 95.1 p. c. was found. On the other hand, the colorimetric estimation with phenylhydrazine recommended by Denner, as well as by Denis and Dunbar, gives useful, although at times rather too high, values (95.1 to 100.9 p. c.), but in this method the unstable character of the reagent is a disadvantage.

It should further be stated that in natural bitter almond oil all these methods only permit of the estimation of the free benzaldehyde, and not of that which is present in combination with hydrocyanic acid. This is shown by the following table:

<table>
<thead>
<tr>
<th></th>
<th>Sample No. 1</th>
<th>Sample No. 2</th>
<th>Sample No. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>3.6 p. c.</td>
<td>2.8 p. c.</td>
<td>2.4 p. c.</td>
</tr>
<tr>
<td>Equivalent quantity of cyanohydrin</td>
<td>17.6 p. c.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. quantity of free benzaldehyde</td>
<td>82.4 p. c.</td>
<td>86.2 p. c.</td>
<td>88.2 p. c.</td>
</tr>
<tr>
<td>Estim. by Ripper's method</td>
<td>81.3 to 82.1 p. c.</td>
<td>80 p. c.; 81.4 p. c.</td>
<td></td>
</tr>
<tr>
<td>Estim. with hydroxylamine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estim. with phenylhydrazine (Denner's or Denis' and Dunbar's method)</td>
<td>83.2 p. c.</td>
<td>83.6 p. c.; 87.2 p. c.</td>
<td>85.2 p. c.</td>
</tr>
</tbody>
</table>

1) Volumetric estimation of the separated sodium hydroxide, with the aid of neutral sodium sulphite. Comp. our Reports April 1904, 48 and October 1904, 119. — 2) Monatsh. f. Chem. 21 (1900), 1079. — 3) Zeitschr. f. anal. Chem. 29 (1890), 228. Also comp. Chem. Zentralbl. 1887, 1411. — 4) Compt. Report October 1909, 155. — 5) We may add to the above that this also applies to Kleber's phenylhydrazine method, which is likewise adapted for the estimation of benzaldehyde (comp. p. 45). In the case of three samples of bitter almond oil containing hydrocyanic acid, of which we estimated the benzaldehyde-content in this manner, we obtained the values given below, which clearly show that only the aldehyde which was present in the oil in the free state has entered into reaction:

<table>
<thead>
<tr>
<th></th>
<th>d_{550}</th>
<th>HCN</th>
<th>Equiv. quant. cyanohydrin</th>
<th>Acid v.</th>
<th>Benzoic acid</th>
<th>Free Benzaldehyde Calc.</th>
<th>Est. by Klebè's method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample a</td>
<td>1.0678</td>
<td>4.95 p. c.</td>
<td>24.4 p. c.</td>
<td>2.7</td>
<td>0.6 p. c.</td>
<td>ca. 75 p. c.</td>
<td>73 p. c.</td>
</tr>
<tr>
<td>Sample b</td>
<td>1.0603</td>
<td>2.79 p. c.</td>
<td>13.3 p. c.</td>
<td>5.3</td>
<td>1.2 p. c.</td>
<td>85,5 p. c.</td>
<td>83 p. c.</td>
</tr>
<tr>
<td>Sample c</td>
<td>1.0848</td>
<td>9.5 p. c.</td>
<td>46.8 p. c.</td>
<td>14.0</td>
<td>3.1 p. c.</td>
<td>50,1 p. c.</td>
<td>50 p. c.</td>
</tr>
</tbody>
</table>
In view of the fact that Sadtler's method also determines only the free benzaldehyde which is present in the bitter almond oil, Dodge calls attention to the illogicality of the requirements of the U. S. A. Pharmacopœia in insisting upon a hydrocyanic acid content of from 2 to 4 p.c., together with a minimum of 85 p.c. benzaldehyde, inasmuch as the hydrocyanic acid percentage demanded represents a proportion of free benzaldehyde varying from 80.3 to 90.1 p.c.

Dodge has worked out yet another method for the quantitative estimation of benzaldehyde. This is based upon Cannizzaro's reaction (reaction of benzaldehyde with potassium hydroxide):

$$2C_6H_5CHO + KOH \rightarrow C_6H_5COOK + C_6H_5CH_2OH.$$

He made tests with alcoholic potash liquor, which showed that the reaction does not proceed quantitatively when the liquor is of less than twice the normal strength. Good results were obtained with a 2.5-normal liquor. With this, 10 cc. is allowed to stand for 24 hours at room-temperature with an exactly-weighed quantity (1 to 2 grams) benzaldehyde (a shorter period of reaction with warming had proved ineffective), after which the unattacked alkali is titrated back with seminormal hydrochloric acid. This blank test makes it possible to ascertain at the same time the exact strength of the potash-liquor. The difference shows how much of the alkali has entered into reaction, expressed in cc. of seminormal potash-liquor. By multiplying the number of cc. with the molecular weight of benzaldehyde (106) and dividing by the quantity of oil employed in the test, the aldehyde-content is obtained.

In the case of pure artificial products, Dodge found this content to be from 99.03 to 100.3 p.c. He rightly lays stress upon the fact that in measuring off the 2.5-normal potash liquor it is necessary to proceed with great care, because so small a difference as 0.05 cc. represents an error of not less than 1 to 2.5 p.c. benzaldehyde. In our opinion this fact alone makes the usefulness of the method somewhat problematical.

In the case of natural bitter almond oil the method gave no useful results, presumably because the saponification of the benzaldehyde-cyanohydrin into mandelic acid was incomplete. Moreover, in this case it is probable that owing to the presence of ammonia when phenolphthaleine is used as an indicator, the terminal point of the reaction is not easily distinguished.

As the odour and taste of the benzaldehyde which is prepared from bitter almond oil are generally regarded as superior to those of even the best artificial product, it is to be presumed that the natural article contains a hitherto unknown constituent. Dodge has attempted to solve this problem by dissolving 60 grams of a bitter almond oil which had been freed from hydrocyanic acid in 100 cc. ether, and diluting the solution with 200 grams concentrated bisulphite solution. The resulting bisulphite compound was filtered off after 18 hours, and washed with ether, the ethereal extract being evaporated in a vacuum-desiccator after being shaken with a little soda-solution. This left a residue of about 0.2 p.c. of a yellow oil, heavier than water, and possessing a pleasant, characteristic odour. So far Dodge has not succeeded in identifying it. Artificial benzaldehyde, when similarly treated, yielded traces of an oil without any clearly-expressed odour.

Almond Oil, Pressed. See Chemical Preparations and Drugs, p. 113.

Ambrette Seed Oil. Ambrette seed of good quality remains extraordinarily scarce, hence the elevated values have been maintained. The demand for ambrette
seed oil has left something to be desired, because it was difficult to persuade consumers to pay the high figures demanded, and also because in artificial ambrette-musk, which has lately been available at such low rates, ambrette seed oil has met with a competitor of which the usefulness should not be underrated.

Angelica Oil. As was to be expected, the result of the distillation of the root of the 1912 crop can only be described as very moderate, and it follows that the high quotations of last year will doubtless continue in force, although naturally, since new oil is available, the market has weakened to some extent. It is said that last autumn considerable new plantations have been laid down in Thuringia; hence the prospects of the new crop are favourable, assuming of course that the young plants have come well through the winter, of which no opinion can yet be formed. Our plantations at Miltitz, which have not been exposed to severe cold, are in a satisfactory condition. But as the residue of 1911 oil was very small, and as the total quantity available will hardly carry us to the end of the year, it is most probable that the present prices will be maintained until the end of the summer. We have distilled large quantities of root, but nevertheless we have no considerable stock of oil left on hand at the present time.

Angelica Seed Oil remains scarce and high in price. The few parcels of suitable seed which have been offered were so dear that it was out of the question to use them for distilling.

From the collected first-runnings of several samples of the distillation Waters of angelica we have caught and examined separately the fraction which passed over first. It constituted a yellow liquid with a slightly acrid odour, and consisted principally of a mixture of a large proportion of methyl and a little ethyl alcohol. We distilled the liquid over phenyl hydrazine, in the course of which manipulation there passed over a colourless body of which the odour had lost its acridity. From the distillation-residue we isolated the osazone of diacetyl (m. p. 239 to 240°). We further identified the the diacetyl from the formation of glyoxalin-silver when ammonia and silver nitrate were added. The methyl alcohol was identified by the violet colour-reaction with magenta-sulphurous acid after oxidation with permanganate1) as well as by preparing the benzoate (b. p. 199 to 202°; d_{150} 1,0894; ester v. 409, calc. 412) and the oxalate (m. p. 54 to 55°). The ethyl alcohol also was identified from the benzoate; b. p. 213 to 213.5°, d_{150} 1,0576, ester v. 372,9 calc. 373,9. The ethyl alcohol which was obtained by saponifying the ethyl benzoate with methyl alcoholic potash gave the iodoform reaction.

The fractions with highest b. p. contain furfurol (colour reaction with aniline acetate) as well as a base with an odour of pyridine.

As a result of this investigation we have therefore been able to establish the presence in the distillation-water of angelica of methyl alcohol, ethyl alcohol, furfurol, diacetyl, and of a base which has not been definitely identified. We do not regard it as impossible that the ethyl alcohol is generated from the green parts of the plant during the storage of the roots.

Angostura Bark Oil. Very little is known with regard to the constants of Angostura bark oil, because the oil is rarely distilled. This fact induces us to communicate here the analytical figures of a distillate prepared by ourselves. A botanical

1) Comp. Apotheker Ztg, 87 (1912), 430.
examination of the bark had shown it to be derived from *Cusparia trifoliata*, Engl. (N. O. *Rutaceae*), and the material was therefore genuine Angostura bark. The yield of oil was 1,03 p.c. The oil was of a pale-brown colour and even in 90 p.c. alcohol (9 vols.) it only gave a turbid solution; \( d_{50} \) 0,9285; \( \alpha_d = 7^\circ 32' \); \( n_{D50} \) 1,50744; acid v. 1,8; ester v. 5,5; ester v. after acet. 35,7.

The low value of the opt. rot. is remarkable, for according to the literary references the limits of value hitherto observed in Angostura bark oil range from — 36 to — 50°.

**Anise Oil, Russian.** According to the information supplied to us by our respondents since the publication of our last *Report*, the Russian anise crop of 1912 was an average one, the area under cultivation (about 3600 dessiatines), having produced about 150 000 poods (= about 2 400 000 kilos). A report from another quarter estimates the output at 190 000 poods, or, say 3 000 000 kilos. The second anise-fair of the season, held at Alexejefka on September 26, was completely spoiled by rain, with the result that the supplies offered were light, and unequal to meet the strong demand for export. Accordingly the prices were high and the fact that neither seed nor oil was carried over into the new season from the 1911 crop assisted in giving a firmer tone to the market. The quality of the new seed, so far as appearance is concerned, proved to be on the whole satisfactory; the oil-yield, although better than in 1911, only reached an average of about 2,6 p.c. Throughout the winter-months prices kept at about the same level at which they stood shortly after the harvest, but lately an upward movement has shown itself, because only a portion of the fields could be prepared for the new season's sowing, the frost having set in very early in October. From this it is concluded that the area under cultivation will suffer a serious reduction. It is therefore probable that before long the prices of anise oil will have to follow suit, for the oil-stocks are by no means heavy enough to prevent the fluctuations in the value of raw material from affecting the position of the market. In any case it is certain that the tendency is very firm at present and that our quotations are fully worthy of attention.

For some time past a foreign firm has been offering anethol under the designation of “anethol 23°”. As in many quarters this designation may lead to the belief that this is a particularly exquisite product with a solidifying point of 23°, we should like to point out that the above qualification can apply only to the melting point. We have already repeatedly ascertained in the case of our own preparation, which as regards all its properties is unsurpassed by any other, that the solidifying point of absolutely pure anethol lies between 21 and 22° and its m. p. between 22,5 and 23°. Theoretically the two values should be in accordance, but the solidifying point is usually found to be a little lower than the m. p., a circumstance which is connected with a slight delay in the beginning of the crystallisation or with cooling below the solidifying point. For the evaluation of anethol the determination of the solidifying point is nevertheless to be preferred to that of the m. p. because the former can be carried out more quickly and with more ease and because its results are absolutely trustworthy, supposing, of course, that the work is always carried on under similar conditions.

For oils containing anethol, such as Russian anise oil, staranise oil, and fennel oil, the determination of the m. p. is not to be recommended, if only for the reason that these oils consist of mixtures of various constituents and therefore do not melt sharply and suddenly throughout the entire mass, but within a certain interval of
temperature. On the other hand their solidifying point is sharp and can be easily observed. We again point out these facts on the present occasion because the proposal is constantly being made from a certain quarter that in the evaluation of these oils the m. p. and not the solidifying point should be taken as the basis.

It goes without saying that our anethol is a least equal to the "23°" anethol referred to above.

**Apple Oil.** According to a communication by C. Thomæ1) the material which he had previously obtained from apple peel by sprinkling with dilute soda solution and extracting with ether2), is not a uniform body, but consists of two fractions with a high and a low m. p. respectively. The first-named fraction has not yet been examined, the latter consists of wax from the peel. The two portions can be separated by repeating the treatment with cold ether, when the waxy substance goes into solution and the body with high m. p. is left behind.

In another experiment green apple peel, without the addition of soda-solution, was extracted for two days with ether at room-temperature. From the evaporated ether a crystalline substance separated out which was filtered off. When this liquid was afterwards evaporated in vacuo, a dusty mass sublimed out, which melted under the warmth of the hand and had a pleasant odour of apples. At an increased temperature a thick, yellow oil passed over which crystallised immediately.

Thomæ also heated the green peel, without adding water, to 150° in an oil-bath in the vacuum of a water-jet pump, whereby he obtained an aqueous distillate containing colourless oil drops with an agreeable perfume. As the temperature increased the liquid began to give an acid reaction. When the oil-bath temperature was at 170 to 180° a white sublimate made its appearance. It consisted chiefly of wax and possessed an exquisite odour of flowers.

**Arnica Oils.** A series of distillates which we have prepared in the course of the last few years from arnica root and from arnica flowers has given us an opportunity of making further observations with regard to the limits of value of the separate constants of these oils. The result was as follows:

Arnica root oil. $d_{150}^{0} 0.984$ to 1.00; $\alpha_D + 0^\circ 25'$ to $- 2^\circ$; $n_{D20}^{150}$ 1,507 to 1,508; acid v. 4 to 10; ester v. 60 to 100; soluble in 7 to 12 vols. of 80 p. c. alcohol and in 0,5 to 6 vols. of 90 p. c. alcohol; in both cases possibly with turbidity.

Arnica flower oil. Butter-like mass, melting to a brownish liquid between 20 to 30° (about). $d_{20}^{0} 0.8905$ to 0,9029; acid v. 62,6 to 127,3; ester v. 22,7 to 32,2.

The oil is very sparingly soluble in alcohol; even with absolute alcohol the solutions are only clear in the beginning.

**Oil of Indian Artemisia vulgaris.** From the Indian Museum at Calcutta we have received a distillate from *Artemisia vulgaris*, L. (*A. indica*, Willd., N. O. Compositæ) which had been prepared at Lebong in the District of Darjeeling (Bengal). The oil was described to us as "Indian Wormwood Oil". Its colour was yellowish with a greenish fluorescence and it had an odour of sage: $d_{150}^{0} 0,9219$; $\alpha_D - 8^\circ 52'$; $n_{D20}^{150}$ 1,46201; acid v. 1,2; ester v. 22,1; ester v. after acet. 55,5; sol. in 1 vol. 80 p. c. alcohol. When more than 5 vols. was added, opalescence ensued and after prolonged standing paraffin crystals separated out from the solution. With semicarbazide we succeeded in separa-

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ting α-thujone from the oil. The semicarbazone had m. p. 186°, and sp. rot. \([α]_D + 64.4°\) (in alcoholic solution). The thujone regenerated from the semicarbazone by means of phthalic anhydride was, singularly enough, inactive. From the odour of the oil it is probable that it contains borneol, but there was not sufficient experimental material available to determine this point.

**Atherosperma Leaf Oil.** Of *Atherosperma moschatum*, Lab. ("Australian sassafras"), a plant belonging to the N. O. *Monimiaceae*, and a native of Victoria, only the oil from the bark was known up to the present\(^1\). The oil from the leaves has only recently been prepared in fairly large quantities by M. E. Scott\(^2\) and has been closely investigated by her. The leaves were distilled two or three days after being gathered, and yielded 1.7 to 2.65 p. c. oil. The fractions which passed over first (about 30 p. c.) were lighter than water, the others were heavier. The crude product is of a yellowish colour, with a clearly perceptible sassafras odour. Its characters are as follow: d 1.027, \([α]_D + 7.5°\), \(n_D 1.5211\). The presence of the following constituents was ascertained: 15 to 20 p. c. α-pinene (b. p. 157 to 158°; hydrochloride m. p. 130°; nitrosochloride, m. p. 103°), 15 to 20 p. c. d-camphor (m. p. 174.5 to 176°; \([α]_D + 40.66°\)), 50 to 60 p. c. methyleugenol (b. p. 251.7°; bromoderivative m. p. about 75°) and 5 to 10 p. c. safrol (b. p. 233°; m. p. 8 to 12°).

**Oil of Backhousia citriodora.** According to a communication by R. C. Cowley\(^3\), Director of the School of Pharmacy at Brisbane, Queensland, it is to be feared that the production of oil of *Backhousia citriodora*, F. v. Muell. (N. O. *Myrtaceae*) will diminish more and more, and that for this reason the hopes which have been awakened in connection with this oil as a raw material for the preparation of citral\(^4\) will probably never be realised. The cause of this decline is that the producers do not consider the distillation of the oil to be a sufficiently lucrative pursuit (comp. our last *Report*, p. 119) and that, moreover, the trees which yield the oil are gradually being exterminated, because the wooded coast-strip between Brisbane and Gympie, which is the only place where the trees are found, is more and more being utilised for other purposes.

The oil-yield is rather small; for instance, 33 cwts. of (green?) leaves and branches afforded only 26 lbs. oil, = 0.703 p. c. In Gildemeister and Hoffmann's *The Volatile Oils*, 1st Ed. p. 538, it is stated that the leaves contain 4 p. c. essential oil.

**Banana Oil.** C. Kleber\(^5\) has recently isolated and investigated the odoriferous principle of the banana. For this purpose he allowed an entire bunch of green bananas to ripen thoroughly, peeled the ripe fruit, crushed it, and, from this highly aromatic material, prepared by steam distillation a few drops of an oil possessing the characteristic odour of bananas. By saponifying with aqueous soda liquor, Kleber succeeded in splitting up the oil into acetic acid (analysis of the silver salt) and into a body with a fusel-oil like odour. The latter he converted from primarily-produced valeraldehyde into valeric acid (analysis of the silver salt), by oxidation with permanganate in alkaline solution. Kleber holds that this investigation proves the occurrence of amylacetate in ripe bananas. In addition the oil contained traces of a body with an odour of phenol.

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\(^1\) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, p. 369.  
\(^2\) Journ. chem. Soc. 101 (1912), 1612.  
\(^3\) Chemist and Druggist 81 (1912), 523, 965.  
\(^4\) Comp. Schimmel's Bericht April 1888, 20; October 1888, 17; *Report* April 1905, 83; October 1905, 44; October 1906, 12.  
\(^5\) Americ. Perfumer 7 (1912), 235.
Although the odour and the taste of bananas clearly remind of the ester in question, and although it is well-known that the aromatic principle of a variety of fruits can be excellently imitated by the aid of synthetic esters, especially amylesters, no proof had yet been given of the presence of amylester in natural products.

The circumstance that it was precisely in bananas, a fruit which in its native country is a highly-esteemed foodstuff and which is also becoming more and more popular in Europe, a fruit moreover of which the harmless character is universally recognised, that amylacetate should be discovered, should be of interest in view of the trouble which has arisen in connection with the use of artificial fruit essences in the manufacture of liqueurs. The expert opinions given in connection with this matter declared in part that artificial fruit essences consisted of amyl-esters which were prepared from fusel oil and were consequently injurious to health.

It is true that no convictions have resulted from these troubles, because the aforesaid expert opinions could not be maintained, but nevertheless these incidents were exceedingly unpleasant for the manufacturers concerned.

The fact that amylacetate can be taken in bananas without any danger to the human health shows that the use of small quantities of synthetic amylesters in essences which serve for the preparation of liqueurs and aerated waters is quite innocuous. Moreover, in examining and judging fruit essences prepared from natural fruit which is known to contain esters, care must now be recommended, for it is quite possible that amylesters may be found to be among the natural constituents of other fruit, as they are of bananas.

In this respect the series of similar investigations which C. Kleber intends to make with other fruit will be of great interest.

**Oil of Sweet Basil.** This article, which was formerly so much in demand for fine perfumery, is scarcely called for at all nowadays, but on the other hand the supplies have also ceased almost entirely. For this reason the price has remained unaltered at its old level.

Roure-Bertrand Fils describe two samples of oil of sweet basil, produced in the island of Mayotta, and possessing the following constants: \( d_{150} 0,9677 \) and 0,9630, \( \alpha_{D} + 0^\circ 58' \) and \( + 0^\circ 56' \), acid v. 1,4 and 0,7, sap. v. 5,6 and 6,3, sol. in 3 and 3,2 vols. and more 80 p. c. alcohol. The samples had the characteristic odour of sweet basil oil, with this difference that it reminded not only of methyl chavicol but also, and fairly distinctly, of anethol.

The constants of the oils are the same as those of Réunion oil.

**Bay Oil.** At last the scarcity of this article has come to an end, and there is now no difficulty in procuring regular supplies of unimpeachable quality. The defects that used to attach to the oil which was formerly imported appear to have been overcome, probably because the manufacturers have now acquired greater practice in distilling. It is true that so far as quality is concerned the West-Indian oils are still inferior to our own oil (which we ceased to distil years ago for lack of supplies of bay-leaves), but this drawback is not specially felt, because those perfumers who are accustomed to use an extra-quality oil are still able to have recourse to our terpene-less bay oil. The latter is not only exceptionally soluble, but it has the additional

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1) *Berichte von Roure-Bertrand Fils*, October 1912, 76.
advantage of a particularly pure and aromatic odour. A few weeks ago we were able to reduce the prices, but it is probable that they will now remain at their present level, as the demand leaves nothing to be desired.

W. C. Fishlock\(^1\) gives particulars on the bay oil and bay rum industry in the islands of St. Thomas and St. John in an article of which we reproduce the outlines as follows:

If it is desired to obtain an oil of good quality, carefully collected leaves must be worked up. It is not easy to procure a uniform raw material, because the *Myrcia* and *Pimenta*-species which are suitable for the preparation of bay oil are most difficult to distinguish from each other. The true parent plant is said to be *Pimenta acris*, Wight, but according to Fishlock there are various varieties which yield the ordinary bay oil of commerce. Particular care must be taken to avoid mixing with the raw material the leaves of the so-called "lemoncilla"\(^2\) because this admixture spoils the whole distillate. Morphologically it is impossible to distinguish the variety know as "lemoncilla" or "false bay" from the common bay shrub; the leaves can only be recognised by their odour. It would appear that the bay-shrub varies greatly, but little is known of the different varieties.

With regard to the cultivation, Fishlock\(^3\) reports, *inter alia*, as follows: The first gathering of leaves can be made when the bay-shrubs have reached the age of five years. The gathering takes place in the dry months: February, March, and April. A ten-year-old tree yields from 60 to 100 lbs. of leaves annually, for which 2 cents per lb. is paid in St. John. The principal producing area includes Porto Rico as well as St. John, but the genuine bay-tree also occurs in Barbuda, Montserrat, Dominica, Saba, Antigua, and other islands. The bay shrub does not grow in St. Thomas. In that island not only the leaves but also the young terminal branchlets are used for distilling purposes. The stills are of copper, of about 200 gallons capacity, and hold about 400 lbs. of green leaves. The still is filled with water to which 35 lbs. of common salt is added, or the distilling-water is mixed with one-third its volume of sea-water. The oil-yield varies according to season, location, and climate. The average quantity of green leaves required to produce a bottle of oil (\(= \frac{1}{6}\)th gallon) is from 130 to 140 lbs., which equals a yield of from about 1,2 to 1,3 p.c.

Bay rum is made either by distilling the bay leaves with rum or spirits of high strength or by mixing bay oil with rum or alcohol. The bay rum obtained by distilling is the best. To prepare it, 400 lbs. green or 200 lbs. dried leaves are mixed in the copper still with 65 gallons Demerara rum, the still being then filled up with water. The distillate constitutes the genuine bay rum of commerce.

The value of a bottle of bay oil in St. Thomas is from 18/- to 20/-, in Porto Rico about 16/-.

Fishlock explains that the reason why the island of St. Thomas is the centre of the bay oil industry is its proximity to the island of St. John, from which, as stated above, the raw material is procured, and furthermore the fact that in St. Thomas the import-duties on alcohol and rum have always been low (from 3 to 6 p. c. *ad val.*). The existence of good shipping facilities in St. Thomas also favours the industry.

In an appendix to the article, H. A. Tempany deals with bay oil distillation in the Leeward Islands. The quality of the oils distilled there is bad, which is chiefly attributable to careless distillation. The light and the heavy fractions of the oil are often

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\(^1\) *West Indian Bulletin* 12 (1912), 513.  
\(^2\) It is probably this variety which yields the so-called "Lemon-scented Bay oil" to which we have referred on previous occasions (*Report* April 1909, 21; October 1909, 29).  
\(^3\) Comp. *Report* October 1912, 25.
sold separately, and it happens occasionally that the light fractions are rejected owing to their being adulterated with petroleum. In the Leeward Islands the oil yield is 26½ fl. oz. per 120 to 140 lbs. of green leaves (= 1½ to 1½ p. c.).

In conclusion it is stated that the leaves of Canella alba, known in Antigua as “false” or “bastard” cinnamon, may be mistaken for bay leaves.

Birch Bud Oil, readily soluble. Owing to its high paraffin-content, birch bud oil as a rule does not give a clear solution either with 80 p. c. (1 to 2 vols.) or with 90 p. c. (0.25 vols.) alcohol, but separates out paraffin. When more of the solvent is added paraffin is invariably separated. As the oil is mostly used in the preparation of birch hair-washes, this circumstance has often caused complaints on the part of our customers. For this reason we have decided to prepare a stearoptene-free oil, which we are placing upon the market under the name of “Birch Bud Oil, readily soluble.” This preparation gives a clear solution with any proportion of 80 p. c. alcohol, and should therefore be sure of meeting with general approval. The other characters of such a stearoptene-free oil are as follow: $d_{15^0} 0.9756$, $\alpha_p - 6^\circ 20'$, $n_{D25^0} 1,50092$, acid v. 2.7, ester v. 56.9, ester v. after acet. 185.0. The paraffin which is obtained as a by-product in the course of manufacture had m. p. 48°. After being recrystallised from alcohol.

Borneo Camphor Oil. The essential oil of the Borneo camphor-tree, Dryobalanops aromatica, Gärtn., N. O. Dipterocarpaceæ, is only very rarely seen in commerce. This fact probably explains why it is that reliable literary references to its chemical constitution are very scanty. It was likewise an inducement to us to make an investigation of the oil and to examine somewhat more closely its chemical constituents. But before giving the results of our investigation, which was made quite recently, we regard it as desirable to make a brief reference to the outcome of earlier researches which in part contradict each other. Martius 9), Pelouze 4), and Gerhardt 5) all declare borneol to be the characteristic constituent of the oil, while Lallemand 4) and Mac Ewan 7) have been unable to detect the presence of this alcohol in the oil. The oil examined by Lallemand, which was derived from Sumatra, may perhaps have contained dipentene; it consisted principally of a body of which the m. p. lay between 260 and 270°, obviously a sesquiterpene; but it is doubtful whether the hydrochloride (m. p. 125°) obtained from this body was a cadinene-derivative. Pelouze’s “borneene” consisted probably in the main of camphene. More recently, van Romburgh 9) has found pinene and d-borneol to be among the constituents of the oil.

The physical characters of the material examined by us, which was derived from Singapore and which was of a dark-brown colour, were as follow: $d_{15^0} 0.9180$, $\alpha_p + 11^\circ 5'$, $n_{D20^0} 1,48847$, sol. in 5 vols. a. m. 90 p. c. alcohol (with slight turbidity), insol. in 10 vols. of 80 p. c. alcohol, acid v. 5.6, ester v. 0, ester v. after acet. 50.5, corresp. to 17.67 p. c. ester $C_{10}H_{17}OCO\cdot CH_3$. Its odour resembled that of turpentine, while at the same time reminding of borneol. When fractionated in vacuo the oil was found to contain large quantities of $\alpha$-pinene and camphene, and from 30 to 35 p. c. of resinous constituents.

The terpenes which pass over first, after being distilled over sodium, possessed the following constants: b. p. 155 to 156°, $d_{15^0} 0.8631$, $\alpha_p + 7^\circ 32'$, $n_{D25^0} 1,46668$. These

constants point to \( \alpha \)-pinene. The nitrosochloride of the fractions in question had m. p. 103°, the corresponding benzylamine base melted at 123 to 124°. The fraction therefore contained \( \beta \)-\( \alpha \)-pinene.

A fraction possessing the b. p. of camphene gave the following constants: \( \text{d}_{150} 0,8639, \alpha_d + 5^°\) 37'. On hydration with glacial acetic-sulphuric acid it afforded a large proportion of \( \text{iso} \)borneol, but in spite of repeated purifications from light petroleum the m. p. of the last-named body remained as low as about 208°. Small quantities of \( \beta \)-pinene were found in a fraction possessing the following physical properties: b. p. 163 to 167°, \( \text{d}_{150} 0,8607, \alpha_d = 0^°\) 20', \( \eta_{d20} 1,47102 \). When treated with permanganate and alkali it yielded in the form of an oxidation-product the characteristic leaflets of sodium nopinate, from which nopinic acid, m. p. 124 to 126°, was obtained. Oxidation of the sodium salt with permanganate in acid solution afforded nopinone, of which the semicarbazone had m. p. 186 to 188°.

The oil contained neither \( p \)-cymene nor phellandrene. The identification of the first-named hydrocarbon was attempted from fractions boiling between 170 and 175° and 175 and 178° respectively, by oxidation with permanganate. Fractions of the same b. p. were tested for phellandrene, but they neither yielded the nitrite nor the oxidation-products characteristic of phellandrene. On the other hand, dipentene was readily identified in fractions with b. p. 175 to 178° (\( \text{d}_{150} 0,8572; \alpha_d = 6^°\) 36'). Bromination in glacial acetic acid solution gave rise to the tetrabromide, m. p. 125 to 126°.

\( d \)-Borneol was found to occur in the following mixture, which distilled over between 55 and 85° (5 mm.). When fractionated once more it congealed in the condenser. Filtered by suction the crude product, when tested for camphor with semicarbazide, proved to be camphor-free. The borneol, after being purified by recrystallisation from light petroleum, indicated the desired m. p., \( \text{viz.} \) 204°. Its chloroform solution was dextrorotatory.

With the object of setting free the borneol from the higher boiling fractions of the oil and from the mother-liquors, these latter were benzoylated with benzoylchloride, with the aid of pyridine. The oil which was driven off in the steam-current by this manipulation, and which was not esterified, proved to consist substantially of \( l \)-\( \alpha \)-terpinene, m. p. 35°. A fraction gave the following constants: \( \text{d}_{150} 0,9379, \alpha_d = 8^°\) 2'. When inoculated under cooling it solidified completely. The resulting phenylurethane had m. p. 112°. After saponification of the residue of steam-distillation no alcohols other than borneol were discovered. In view of the fact that during the fractionation of Borneo-camphor oil a great deal of resin was left behind in the residue, we considered it advisable to rectify a little of the oil by steam-distillation in order to test the oil-fractions with the highest b. p. Those oil-fractions which entered into consideration for testing for safrol and other bodies of high b. p. were further resolved, but it was then shown that no constituents of the odour and b. p. of safrol, 230 to 235° were contained in them. The highest boiling fractions b. p. 102 to 112° (4 to 5 mm.), consisted only of sesquiterpenes. None of them, when warmed, reacted with strong formic acid; hence no sesquiterpene alcohols were present. One fraction was found to possess the following constants: b. p. 102° (4 to 5 mm), 256 to 260° (ord. press.), \( \text{d}_{150} 0,9200, \alpha_d = 137^°\) 12', \( \eta_{d20} 1,50111 \). From the analysis and from treatment with sodium it was evident that the fraction contained no oxygenated constituents.

<table>
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<th>Substances</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
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<td>0,2073</td>
<td>0,2073</td>
</tr>
<tr>
<td>C</td>
<td>88,29</td>
<td>88,23</td>
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<tr>
<td>H</td>
<td>11,70</td>
<td>11,76</td>
</tr>
<tr>
<td>Subtotal</td>
<td>1,0000</td>
<td>0,9968</td>
</tr>
</tbody>
</table>

3
Although the constants point to cadinene, no solid derivatives of this sesquiterpene were obtainable. With the object of preparing the dihydrochloride the oil was saturated both in ether and in glacial acetic acid solution with hydrochloric acid gas, and left in contact therewith for a long time. Neither crystalline products nor a solid nitrosocloride, nitrosate, or bromide was obtained in either case. No characteristic oxidation-products were isolated by oxidation with permanganate, either in acetone solution or in dilute aqueous solutions. The sesquiterpene also differs from the cadinene by its exceptionally slight degree of solubility in glacial acetic acid.

As a result of the examination detailed above it may be taken that the oil under examination contained about 35 p. c. terpenes, consisting of \(\alpha\)-pinene, camphene, \(\beta\)-pinene, and dipentene; about 10 p. c. alcoholic constituents, borneol and \(\alpha\)-terpineol (m. p. 35\(^\circ\)), about 20 p. c. sesquiterpenes, and approximately 35 p. c. resin.

**Buchu Leaf Oil.** The scarcity continues and our stock of oil with a normal buchu-camphor content has now been reduced to a few kilos. Unfortunately the difficulties in the way of procuring suitable material for distilling still remain insurmountable.

W. Mansfield\(^1\) has found several samples of buchu leaves to contain an admixture (up to 17 p. c.) of the leaves of *Diosma fragrans*, which is known as "Klip-buchu".

**Oil of Barosma venusta.** From the dry leaves of *Barosma venusta*\(^2\) Ecll. et Zeyh. H. R. Jensen\(^3\) has distilled 1,1 p. c. essential oil possessing the following constants: \(d_{15}^{15.25} 0.8839\), \(\alpha_{D}^{20} +0^\circ 30\), \(n_{D}^{20} 1.4967\), acid v. 2.4, sap. v. 13.4, sap. v. after acet. 52.8, phenol-content 16 p. c.; 4 p. c. of the oil combined with neutral sulphite. Jensen found the oil to contain 35 p. c. of a terpene possessing the following characters: b. p. about 66.5\(^\circ\) at 15 to 18 mm., \(d_{15}^{20} 0.790\), \(n_{D}^{20} 1.4778\). It did not boil without decomposition under ordinary pressure and when hydrated it afforded an alcohol of which the acetic ester had an odour of linalyl acetate. It resinifies with extreme rapidity when exposed to air. All these properties agree with those of myrcene. Jensen also assumes that, in addition to the above, the oil contains the following constituents: methylchavicol (conversion into anethol), the acetate of myrcenol or of an isomeride of myrcenol, chavicol (n. 1.538; green coloration with ferric chloride), and perhaps an olefinic sesquiterpene. Diosphenol was not present in the oil.

A new species of *Barosma* has been described as *B. Peglerae* by R. A. Dümmer\(^4\). It occurs on grassy slopes in the Eastern parts of South Africa. The leaves show some resemblance to those of *B. lanceolata*, but they differ from the latter in their shape, which is broader and elliptical, and by the presence of oil-cells on the lower surface of the leaf. It is not yet possible to judge whether the leaves possess any economic value.

**Cajuput Oil.** We have received from our source of supply on the island of Buru regular supplies of the well-tried quality of oil, but generally speaking business has dragged greatly, and transactions of any importance were rare. The greater part of the production of cajuput oil continues to be consumed in the United States.

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\(^1\) *Chemist and Druggist* 51 (1912), 546.
\(^2\) *Comp. Report* October 1911, 23.
\(^3\) *Pharmaceutical Journal* 90 (1913), 60.
\(^4\) *New Bull.*, 1912, 326.
According to the British Pharmacopœia the sp. gr. of cajuput oil should be 0,922 to 0,930 (15,5°), a demand which has already repeatedly caused complaints, because it is not in accordance with fact. It has been pointed out in various quarters that the sp. gr. of normal oils may fall as low as 0,919 and in England efforts have been made to ensure that in a new edition of the Pharmacopœia this fact shall be recognised. Until that edition appears, however, the prescriptions of the existing Pharmacopœia must be followed, and this may occasionally lead to the “doctoring” of an oil with too low a sp. gr.

Such an oil Umney 1) believes to have met with. Its sp. gr. was 0,924 and in this respect it therefore complied with the B. P. requirements, but singularly enough the oil was dextrorotatory (αD about +2°) whereas ordinarily cajuput oil is laevorotatory. In addition, the oil contained remarkably few low-boiling fractions, for up to 185° only 14 p.c. of it passed over, as compared with 50 p.c. in a normal oil. As a consequence, the cineol-content was also very low, for instead of 60 p.c., as in a normal oil, the phosphoric acid method only indicated 14 p.c. Umney is of opinion that the oil was originally normal, but that it had been fractionated and its sp. gr. increased by the rejection of the first fraction in order to make it conform with the B. P. standard. In the course of this manipulation it was unavoidable that, along with the terpenes, a considerable quantity of cineol (which boils within very nearly the same range as the terpenic constituents) was lost.

Oil of Calamintha Nepeta. In the course of the summer of last year, oil has been distilled in Sicily from the green (?) herb of Calamintha Nepeta, Link et Hoffm. (N. O. Labiatae). The yield was 0,1426 p.c. and the oil, which was of a brownish colour, had an odour reminding of oil of pennyroyal 2). Its constants were as follow: d150 0,9249, αD +170° 48', acid v. 1,4, sap. v. 12,6, ester v. after acet. 48,5, sol. in 3 vols. 70 p.c., 2 vols. 75 p.c., and 0,5 vols. 80 p.c. alcohol. When more 70 or 75 p.c. alcohol is added the mixture turns cloudy or becomes opalescent. The estimation of pulegone with neutral sodium sulphite gave a pulegone content of 20 p.c. In addition to pulegone the oil probably contains menthone. This is indicated by the fact that the ester value of the reduced and subsequently acetylated oil was 190,4, that is to say considerably in excess of that of the original oil. The reduced oil, owing to the formation of l-menthol from the pulegone and the menthone, was laevorotatory (αD — 18°).

We ourselves have found the oil of Calamintha Nepeta to possess the following constants: d150 0,9271 to 0,9395, αD +2° 50' to +6° 49', nD20, 1,48441 to 1,48920, ester v. 5,4 to 14,6. Pulegone content 45 p.c. (one estimation only) 2).

Roure-Bertrand Fils give the following synonyms for Calamintha Nepeta, Link et Hoffm.: C. parviflora, Lamk., C. trichotoma, Mœnch, Melissa Nepeta, L., M. cretica, All., and Thymus Nepeta, Sm.

Calamus Oil. A change has made itself felt in the position of this article, inasmuch as it has been extremely difficult during the last few months to procure calamus root of good quality, and for the few parcels which have been placed upon the market high prices were demanded. For this reason we have been compelled to advance our quotations, and we shall be unable to make offers for contracts of any importance until the future of the market has become somewhat clearer and until it is again possible to secure considerable supplies of distilling material.

1) Perfum. and Essent. oil Record 3 (1912), 243. 2) Berichte von Roure-Bertrand Fils, October 1912, 73. 3) Report October 1906, 14; October 1911, 24; also comp. Report October 1902, 51; April 1903, 50.
**Camphor Oil.** As in previous years, the bulk of the crude camphor oil brought to market in Japan in the course of the winter was shipped to the United States, where great value is notoriously attached to the preparation on a wholesale scale of a fraction with a sp. gr. 1.07, which is used under the name of "artificial sassafras oil" for all manner of technical purposes. As for ourselves, we are primarily interested in the manufacture of pure safrol, and we have also received several large shipments of crude oil, the cost of which figures out at a little less money than that of previous imports. In spite of this fact, we have been unable to lower the quotations of our two by-products, "light" and "heavy" camphor oil, which is testimony to the manifold technical purposes for which the two articles are employed. The use of the oils in question has in no way been restricted by the fall in the value of turpentine oil. Considerable quantities of them are used up in the manufacture of cheap disinfectants, a branch of industry which has lately acquired such a great importance.

In the Financial and Economic Annual of Japan\(^1\), published by the Imperial Department of Finance at Tokio, we find the following statistical data on the production of camphor and camphor oil in Japan during the years 1901 to 1910.

<table>
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<th>Year</th>
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<th>Camphor oil</th>
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<td></td>
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<td>587040</td>
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The exports of camphor from Japan in the last decade were as follows\(^3\):—

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<tr>
<th>Year</th>
<th>Yen</th>
<th>Yen</th>
<th>Yen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1901</td>
<td>1905</td>
<td>1909</td>
</tr>
<tr>
<td></td>
<td>3904973</td>
<td>2566233</td>
<td>3469398</td>
</tr>
<tr>
<td>1902</td>
<td>3404833</td>
<td>3632785</td>
<td>2964369</td>
</tr>
<tr>
<td>1903</td>
<td>3537844</td>
<td>5026858</td>
<td>3143084</td>
</tr>
<tr>
<td>1904</td>
<td>3168197</td>
<td>2063410</td>
<td></td>
</tr>
</tbody>
</table>

P. 191 of the same Annual contains a statistical review of the camphor production in Formosa:

<table>
<thead>
<tr>
<th>Year</th>
<th>Camphor</th>
<th>Camphor oil</th>
<th>Camphor</th>
<th>Camphor oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kin</td>
<td>Kin</td>
<td>Kin</td>
<td>Kin</td>
</tr>
<tr>
<td>1901</td>
<td>3667887</td>
<td>2587186</td>
<td>1906</td>
<td>3252408</td>
</tr>
<tr>
<td>1902</td>
<td>3148742</td>
<td>2388135</td>
<td>1907</td>
<td>3914598</td>
</tr>
<tr>
<td>1903</td>
<td>3595814</td>
<td>2678794</td>
<td>1908</td>
<td>3354970</td>
</tr>
<tr>
<td>1904</td>
<td>3540953</td>
<td>2805809</td>
<td>1909</td>
<td>3537712</td>
</tr>
<tr>
<td>1905</td>
<td>2865117</td>
<td>2373788</td>
<td>1910</td>
<td>3560642</td>
</tr>
</tbody>
</table>

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No further official statistics on the camphor production in Formosa are at our disposal, but in a Report by the British Consul\(^1\) at Tamsui we find a statement according to which the Monopoly Bureau estimated the output of refined camphor in Formosa during the year 1911 at 7,267,000 lbs.

The exports of camphor from Formosa 1911 amounted to 5,613,718 lbs., of which 2,374,666 lbs. went to Germany, 2,039,500 lbs. to the United States, 562,267 lbs. to France and 472,000 lbs. to the United Kingdom. The exports showed a reduction of 872,554 lbs. compared with those of the previous year.

Further statistics relating to the camphor exports from Formosa are given on p. 193 of the Annual referred to:

<table>
<thead>
<tr>
<th>Year</th>
<th>Camphor (Yen)</th>
<th>Camphor (Yen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1902</td>
<td>2,849,132</td>
<td>1,907</td>
</tr>
<tr>
<td>1903</td>
<td>2,518,305</td>
<td>1,710,493</td>
</tr>
<tr>
<td>1904</td>
<td>2,199,320</td>
<td>4,377,816</td>
</tr>
<tr>
<td>1905</td>
<td>2,052,933</td>
<td>3,932,750</td>
</tr>
<tr>
<td>1906</td>
<td>2,222,729</td>
<td>3,463,208</td>
</tr>
</tbody>
</table>

Both in this *Report* and in one of the *Diplomatic and Consular Reports*\(^2\) there are references to the distillation of camphor leaves, which it is intended to take up in Formosa quite shortly. The leaves of young trees are collected for this purpose. Leaves without branches give the best results: 1,3 p.c. camphor and 0,4 p.c. camphor oil. It is the intention, beginning with the years 1913 and 1914, to plant for 12 years in succession about 3,000 acres yearly with young camphor trees. At the end of that time it is estimated that the annual production of the area planted will be about 6,500,000 lbs. of camphor and the same quantity of camphor oil. Possibly the project of these plantations may be due to an impending shortage of distilling material, to which reference is made in a Dutch official journal\(^3\). It is there said that the prospects of the camphor industry in Formosa are rather bad. The camphor forests in the interior, far from being almost inexhaustible, as was formerly assumed, will only be able to produce camphor for about 20 years at the longest. The experience of planting has been bad. The belief that the trees would commence to yield after 7 or 8 years and would be full-grown in about 30 years has not been confirmed. On the other hand, the camphor-forests in Southern China are much more extensive than had hitherto been thought, and it is anticipated that as soon as order has been restored in China the camphor-production of that country will rule the market of the world.

From a communication to the *Chemische Industrie*\(^4\) we also learn that camphor refining on a large scale has been commenced at Taikolen, the capital of Formosa, whereas formerly all the crude camphor was shipped by the State Monopoly Bureau of the Island of Formosa to private refineries in Japan. Since September 1911 100,000 lbs. have already been refined at Taikolen in works fitted out with modern plant, and it is expected that five times this quantity will be produced in the fiscal year ending March 1\(^{st}\), 1913. Probably the improvements of the refining industry to which reference is made in the afore-mentioned Report of the British Consul at Tamsui apply to this project. It is said there that at present the oil-yield is 48 p.c., from which a camphor of 93 p.c. purity is prepared.

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We may here also refer to an article which has appeared in an American trade journal, according to which there are two varieties of camphor tree in Formosa\(^1\) of which one is said to yield only camphor oil and the other only camphor, while between them, it is said, all possible subvarieties exist. We are still waiting for an explanation of this remarkable phenomenon. Possibly the differences here referred to are not botanical, but have a physiological basis. The statement is not new; we have already referred to it several years ago\(^3\). Subsequently we have also mentioned the remarkable experiences which have been made in the camphor-producing industry and which indicate that either the camphor-producing trees are imperfectly known botanically or that not all the specimens of the separate species afford camphor\(^4\).

In the Dutch commercial paper\(^5\) mentioned above we find a short notice of new plantations of camphor trees. It refers to the Idzu region (Japan) and to the Bonin-islands off the coast of Japan. The soil and climate of these islands are said to be particularly favourable to camphor cultivation. Experiments in planting have been made since the year 1908, two plantations having been laid down, one of 122.5 acres at Oshima (Vries Island) and one of 208.05 acres at Hachijo. The results have been very favourable, the trees flourished, and began to yield camphor after only 4 years. In 1912 a beginning was made with the distillation of the leaves, and the camphor obtained from these is said to be of good quality.

Utz\(^6\) claims to have discovered a method for differentiating camphor oil from turpentine. When American, French, Greek, or Spanish turpentine oil is shaken up with half its volume of solution of stannic chloride, the oil-layer appears to be colourless and the reagent-layer yellow; with camphor oil and pine tar oil the oil appears orange to blood-red, the reagent blood-red. A differentiation between pine tar oil and camphor oil is based upon the difference in their behaviour towards sodium and potassium hydroxides. In contact with pine tar oil these reagents after some time become covered with a brown layer, whereas with camphor oil they remain colourless even after 84 hours or at most assume a very faint yellow tinge.

**Cananga Oil.** In the course of the winter a fairly active trade was developed in cananga oil at rising prices, as the cheap second-hand stocks had been used up. It appears, however, that the upward movement has been determined less by urgent European demand, than by the way in which the dealers in Java outbid each other in their purchases. Increased consumption, however, also accounts in part for the greater firmness. At the present moment the distillers in Java continue to ask very high prices, but if, owing to the remunerative rates, over-production should set in (as has happened before), the effect thereof will no doubt make itself felt in an early weakening of the market. It will then depend upon the consumption whether, and to what extent, prices will recede. For the present, as stated, the article remains extremely firm, and we should say that the possibility to which we have referred is still in the far-distant future. Meticulous care and control continue to be required when making purchases, for the high prices are only too tempting to cause the natives to increase their output by malpractices. It is true, however, that neither in our imports for our own considerable requirements, nor in our analyses made for friendly firms, have we met with a

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\(^1\) Oil, Paint and Drug Reporter 82 (1912), No. 10, p. 48.  
\(^2\) Comp. Report October 1907, 23.  
\(^3\) Comp. Report April 1906, 23; April 1911, 37.  
\(^4\) Handelsberichten (the Hague) 6 (1913), 979.  
\(^5\) Farbenzeitung 17 (1912), 2105; Chem. Zentralbl. 1912, II. 872.
single instance of adulteration lately, and we believe that well-reputed exporters, who have a long experience of the article, always take the necessary care when buying.

Owing to the regularity of our purchases we are always in a position to supply at a moment's notice oil of the finest quality, tested by ourselves, either from our own warehouse or from the various European ports.

**Caraway Oil.** During the last six months the course of the caraway market has undergone a change which no one had expected and which has been a severe disappointment to many speculators. It will be remembered that the total result of the 1912 crop was barely 25,000 bales: the smallest yield on record. But those who concluded therefrom that prices would rise have made an enormous mistake, for whereas after the exceptionally heavy crop of 1911 (224,419 bales) the prices advanced from about 11 Fl. to 20 Fl., after the garnering of last year's scanty outturn they gradually fell to about 14.50 Fl. The reason of this was that in 1911 consumers generally had overbought, and that at times certain manufacturers, while laying in their supplies, caused a senseless boom in the quotations which, in view of the ample crop, must in the end lead to a reaction. Even at the present time there are in existence stocks of caraway oil from the 1911 season which stand in at high rates, and if the prices have not receded to the extent which might have been expected, this is no doubt due to the general endeavour of the principal foreign manufacturers to rid themselves of their holdings, if possible, without loss. Moreover, it is said that the market is practically cleared of caraway seed with a satisfactory oil-content, and it does not pay to work up parcels which are deficient in oil. So far no official reports on the condition of the caraway fields in the various producing districts are available, but we hear from our correspondents that the young plants have come well through the winter and that therefore the prospects are just now very favourable. The price of new seed has consequently for the time being fallen as low as 14 Fl.

**Cardamom Oil.** It need hardly be mentioned that the abnormal prices of all varieties of cardamoms have been the reverse of instrumental in imparting animation to the cardamom oil business, for naturally the consumers hesitate very seriously before paying 220 £ per kilo for an article which formerly cost about 100 £ per kilo. Our correspondents are of opinion that there is no prospect of any improvement in the future, for the plantations are dwindling more and more, the profitable rubber-industry being everywhere preferred to the cultivation of cardamoms. In the year 1912 the exports of Ceylon cardamoms of all descriptions amounted to 476,011 lbs., as compared with 564,819 lbs. in the previous year. These figures are evidence of a serious falling-off in the production. The export statistics for the years 1901 to 1911 are given on p. 33 of our Report of October 1912. From these it appears that the production of cardamoms in Ceylon has fallen by about 50 p.c. within the last decade.

**Cascarilla Oil.** Opportunities of finding raw material for distilling purposes only occur rarely. Most of the cascarilla bark is now sent direct from Honduras to the United States, and this fact makes it rather difficult to secure supplies here. The price of oil is not likely to fall below its present level.

**Cassia Oil.** The market-prices of 80 to 85 p.c. cassia oil have fluctuated since the middle of September of last year as shown below:
1st October 1912 3/6½ „  
15th „ 1912 3/6 „  
1st November 1912 3/6 „  
15th „ 1912 3/6 „  
1st December 1912 3/6 „  
15th „ 1912 3/5½ „  

1st January 1913 3/5½ cif.  
15th „ 1913 3/5 „  
1st February 1913 3/4½ „  
15th „ 1913 3/5 „  
1st March 1913 3/3 „  
15th „ 1913 3/4 „

These figures show that the irregular course of prices in the summer of 1912 has been succeeded by a fall in values, which, however, has been restricted within narrow limits. At present the tendency does not point to a further weakening of the market and it therefore appears to be advisable to cover requirements for the next few months, inasmuch as business is brisk, and a return towards higher rates may easily take place.

Several years ago 1) we pointed out that cassia oils adulterated with colophony were continually being placed upon the market, and that even in oils with a high aldehyde-content this form of sophistication was observable.

As already stated by us at the time, such oils show a higher proportion of distillation-residue (over 11 p. c.), and a higher acid value than do pure oils; moreover, when the sophisticated oils are dissolved in three parts of 70 p. c. alcohol with a saturated solution of lead acetate in alcohol of similar strength, a precipitate is thrown down, whereas no precipitate occurs in the absence of colophony. We endeavoured to put a stop to the supply of adulterated oils by placing in the hands of our Hong-Kong friends the necessary means and instructions to enable them to check the adulteration in the country of production itself. Much to our satisfaction we were soon able to ascertain an improvement in the quality of the oils 2). In spite of all, however, we were unable to prevent the occasional supply to us of qualities which, while showing an aldehyde-content of from 80 to 85 p. c., did not stand the lead-acetate test, and this occasionally caused an animated correspondence between our Hong-Kong friends and ourselves. Such a correspondence took place recently, when we were informed that, try as much as they might, oils which stood the test, i.e. which were entirely free from colophony, were at times unobtainable.

We think that the incomplete result of our endeavours is due to the fact that the insistence upon a cassia oil entirely free from colophony is not so general as would be desirable. Buyers content themselves with an oil containing from 80 to 85 p. c. of aldehyde, without enquiring whether or no it contains small proportions of colophony. In consequence the Chinese are able to dispose of their oil when it contains colophony, and this pays them better than if they were compelled to sell an entirely pure oil at the same price.

It therefore affords us much satisfaction to observe that, according to all appearance, buyers in England are also about to take energetic measures against the malpractice in question. An English journal 3) has taken up the movement for the suppression of this form of adulteration. It starts from the assertion that cassia oil containing from 80 to 85 p. c. of aldehyde very often also contains colophony (rosin) and that from this it may be indirectly inferred (and may be surmised from the fact that samples with an aldehyde-content of from 88 to 93 p. c. are met with), that the natural oil is probably of an aldehyde value of well over 85 p. c. The question has become parti-

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cularly acute in England because parcels of cassia oil shipped to the United States have recently been refused admission in New York, in spite of their adequate aldehyde-value (80 to 85 p.c.) on the ground that they contained rosin.

We should rejoice if the joint efforts of all the parties interested were at last, to succeed to put a stop to this form of adulteration and we shall be glad to contribute our share towards a betterment of the existing conditions, the more so because it was our firm which introduced the method of estimating the value of cassia oil). But judging from our present experiences in combating the adulteration in question we cannot take too optimistic a view of the future.

**Cedarwood Oil.** In spite of the fact that we manufacture this important oil on the largest possible scale, we have been unable always to meet the requirements of our customers. Even the increase in price which has taken place since our last Report has done nothing to lessen the demand. Whoever has become accustomed to our distillate finds himself unable to do without it, and for this reason our brand has nothing to fear from the competition of the cheap American oil, which is only good enough where no particular importance is attached to the factor of odour. We are informed that the American lead-pencil works, where the distillation of cedarwood oil is a by-product, have recently raised their quotations to a not inconsiderable extent.

**Celery Oil.** In view of the enormous prices which have for a long time past been quoted for celery seed, it is of course out of the question to work up considerable parcels, as we were formerly in the habit of doing. On the contrary, we have now to depend upon special occasional purchases, but such lots are still to be found here and there. Prices have advanced repeatedly and remain exceedingly firm. Compared with celery seed oil, our celery oil distilled from the green herb grown in our Milititz plantations is well worth its price. It has gained a large circle of customers among the manufacturers of all sorts of comestibles.

On the resolution of selinene, see p. 137.

**Cinnamomum Oils.** In our Report of April 1905 (p. 83) we described an oil which had been prepared from the leaves of a tree grown in the grounds of the Villa Rothschild at Cannes. According to the information supplied to us at the time the tree was identified as *Laurus Camphora*, L., but the wholly different character of the oil from true camphor-leaf oil made it probable that the tree in question belonged to a different species of *Cinnamomum*, and this view was confirmed by a careful botanical examination which was subsequently made, when *Cinnamomum glanduliferum*, Meissn. was established to be the parent-plant. We again give below a brief description of the oil, which was colourless, with a pronounced odour of cardamoms. Constants: \(d_{150} 0,9058, \alpha_D 26^\circ 12', n_D 1,46803\), acid v. 0,34, ester v. 8,82, ester v. after acct. 46,9, sol. in 1 vol. a. m. 80 p. c. alcohol. The following constituents were found to be present: pinene, camphene (?), about 10 p. c. \(l\alpha\)-terpineol (m. p. 35\(^\circ\)), and especially cineol.

A sample which was sent to us a few years later showed similar characters: \(d_{150} 0,9031, \alpha_D 24^\circ 27',\) acid v. 0,9, ester v. 18,4, ester v. after acct. 55,3, sol. in 1,5 vols. a. m. 80 p. c. alcohol.

1) *Schimmel's Bericht* April 1890, 12; October 1890, 18.
It is a remarkable fact that no camphor was found to exist in these oils, although R. S. Pearson of Dehra Dun had obtained from the leaves of Cinnamomum glanduliferum a camphor which was clearly identical with the Japanese commercial product. We cannot explain the reason of this difference; possibly, in the second case, hybridisation may account for it, seeing that we recently received from Cannes an oil which was the product of a hybrid of Cinnamomum Camphora, Nees et Eberm. and C. glanduliferum, Meissn., growing in the garden of the Villa Flora, there. The last-named oil constitutes a liquid with a strong admixture of camphor. After separating and removing the camphor (about 58 p. c.; m. p. 175°; \([\alpha]_D + 41,66°\) est. in 12,2 p. c. alcoholic solution; oxime m. p. 119) the liquid portion was further investigated with the following result: \(d_{150} 1,0465, \alpha_D + 34° 24'\), acid v. 1,0, ester v. 23,3, ester v. after acet. 46,2, sol. in 0,8 vols. 80 p. c. alcohol, when more than 3 vols. of solvent is added, opalescence ensues. When subjected to fractional distillation further considerable quantities of camphor separated out from the liquid, but this distillate (which in other respects resembled Japanese camphor), contained no safrol; a result which agreed with our experience of certain other camphor leaf oils).

Cinnamon Oil, Ceylon. As the prices of Ceylon cinnamon chips, the principal raw material from which this oil is distilled, have undergone but few fluctuations last year, our quotations for Ceylon cinnamon oil have remained steady. Our sales have reached dimensions never before attained, which proves that our exquisite quality is capable of holding its own against every competitor in the matter of price as well as in other respects. The exports of cinnamon chips from Ceylon in the year 1912 amounted to 2349944 lbs., of which over 600000 lbs. went to Germany.

We are now able to complete statements which we made in our Report of November 1908 (p. 41) on the constitution of Seychelles cinnamon-bark oil, by the following particulars: — We examined the first runnings of an oil which had first been fractionated in vacuo and afterwards at atmospheric pressure. Treatment with magenta-sulphurous acid showed the fractions which first passed over to contain small proportions of aldehydes. These were removed by means of bisulphite.

A fraction with b. p. 148 to 155°, a hydrocarbon (\(d_{150} 0,8539; \alpha_D — 17° 2'\); \(n_{D20} 1,47220)\), yielded a nitrosochloride, dec. p. 86 to 87°. The decomposition took place suddenly and violently. With benzylamine traces of a body with m. p. 104 to 109° were obtained as a product of conversion. In view of the readiness with which the nitrosochrome decomposes it is questionable whether the compound can be regarded as a nitrol benzylamine. Camphene could be detected in a fraction with b. p. 159 to 163° (\(d_{150} 0,8563; \alpha_D — 17° 51'\); \(n_{D20} 1,47238)\) by treating with glacial acetic-sulphuric acid. Saponification of the fractions of the reaction-product which boiled in vacuo between 70 and 80° afforded solid isoborneol which, when purified from light petroleum, melted between 209 and 210°.

The fractions boiling between 163 and 167° (\(d_{150} 0,8583; \alpha_D — 24° 20'\); \(n_{D20} 1,47279)\) consisted principally of \(\beta\)-pinene. When oxidised with permanganate in the presence of alkali they yielded nopinic acid, m. p. 125 to 126°.

We are able to confirm our previous statements with regard to the presence in Seychelles oil of \(\beta\)-phellandrene. Fractions with b. p. 36° (3 mm.) and rotation \(\alpha_D — 22° 20'\)

afforded a nitrate with m.p. 103°, of which the chloroform solution turned the polarised ray of light to the right.

Very minute quantities of l-limonene were present in fractions of the same boiling-point. The purified nitrosochloride had m.p. 103 to 104° and with piperidine was converted into nitrolpiperidine, m.p. 93°.

Terpinene did not occur in the fractions boiling between 177 and 179° (d_{150} 0,8560; \( \alpha_d = 17^\circ 4' \)). It could neither be identified from the nitrosite nor from its oxidation-products or its dihydrochloride.

The fractions of the experimental material which were the last to pass over gave with bisulphite-liquor small quantities of a solid separation. By fractionating the aldehyde-free oil we arrived at a fraction with a linalool-like odour and with the following physical characters: b.p. 62 to 63° (3 mm.), 196 to 201° (ord. press.), d_{150} 0,8813, \( \alpha_d = 6^\circ 8' \). When gently warmed with strong formic acid it decomposed with turbidity, as a result of the elimination of water and the formation of terpenes. Although the fraction which obviously contained an alcohol was left in contact with phenylisocyanate for 5 days, only small proportions of a phenylurethane with m.p. 59 to 62° and very difficult to purify, were obtainable. But it is nevertheless probable that this was linalool.

The aldehyde which was recovered from the purified bisulphite-compound had the odour of a higher fatty aldehyde: it was probably nonylaldehyde which, as is well-known, is also a constituent of Ceylon cinnamon oil.

In the resolution of the bisulphite compound of the aldehyde, which was found to occur in the fractions with the lowest b.p., the unmistakable odour of benzaldehyde was observed. The semicarbazone which was prepared melted between 212 and 214° and gave no depression of m.p. with benzaldehyde semicarbazone.

From the above investigation it is evident that Seychelles cinnamon oil possesses the same constituents as Ceylon cinnamon oil. If correspondingly larger quantities of raw material were worked up, it is probable that the constituents of Ceylon oil which have so far not been found present in Seychelles oil would be shown also to occur therein.

**Citronella Oil.** It is a fact that since the publication of our Report of October 1912 the market in Ceylon citronella oil has become somewhat quieter, but in spite of this prices have remained very firm, and continue at this moment to be quoted at from 17 d. to 18 d. p. lb., a figure which, measured by the old standards, is really very high. It would appear that we shall have to reckon with approximately the same conditions of price in the future, for as soon as there is even the slightest sign of a downward tendency such a pressure of orders is felt that the Ceylon traders and exporters are able to dispose of their supplies at once, after which they are in a position to raise their demands once more in the twinkling of an eye, with the result that shortly afterwards the values, as a rule, are back to their previous level, if not above it.

According to official returns the exports have been as follows:—

<table>
<thead>
<tr>
<th>Year</th>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>1 420 306</td>
</tr>
<tr>
<td>1911</td>
<td>1 574 965</td>
</tr>
<tr>
<td>1910</td>
<td>1 762 919</td>
</tr>
</tbody>
</table>

So far, however, the export figures for the current year warrant the belief that the steady decline in exports shown in the above table has reached its nadir, for between January 1st and February 17th, 1913, 120948 lbs. have already been shipped, against 40 581 lbs. in the corresponding period of 1912. It may be concluded from these
figures that we may either expect a considerable increase in the oil-supplies this year, or that the native traders last year intentionally kept back large quantities in the interior of Ceylon (as they were reported to be doing), in order to support the market as far as they could by steadily representing the output to be small, and then disposing of the small supplies brought forward at full prices. The figures quoted above show that this manoeuvre has been successful, and the very marked increase in the exports during the first few weeks of the present year would thus be explained. It need hardly be added that in such circumstances it is difficult to form an opinion of the future course of the market.

*Java Citronella Oil* has become much dearer in the period under review. The arrivals remain comparatively small and are steadily taken up by the consumption at full rates. No doubt the market will remain firm so long as this oil is employed in the chemical manufacturing industry in such quantities as has been the case all along of late.

In our last *Report* (p. 40) we described several methods which have been recommended for the separate estimation of geraniol and citronellal in citronella oil, and in the course of this notice we referred to the process devised by V. Boulez which at the time had been communicated to us privately by the author. Boulez has now also published his method in the *Bulletin de la Société chimique de France* [IV. 11 (1912), 915].

In the meantime we have estimated the geraniol and citronellal contents of another series of citronella oils according to various methods, and in the following table we summarise the results of our investigations:—

<table>
<thead>
<tr>
<th>Nr.</th>
<th>d₁₅₀</th>
<th>α₀</th>
<th>So-called total geraniol (est. by acet.)</th>
<th>Geraniol (phthalic anhydride method)</th>
<th>Citronellal Phenyl-hydrazine method (Kleber)</th>
<th>Oximation method (Dupont and Labaune)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0,8913</td>
<td>−2°15'</td>
<td>85,4 p.c.</td>
<td>35,3 p.c.</td>
<td>36,0 p.c.</td>
<td>36,6 p.c.</td>
</tr>
<tr>
<td>2</td>
<td>0,8859</td>
<td>−1°45'</td>
<td>87,6</td>
<td>35,3</td>
<td>40,0</td>
<td>45,2</td>
</tr>
<tr>
<td>3</td>
<td>0,8866</td>
<td>−1°35'</td>
<td>88,7</td>
<td>36,4</td>
<td>40,0</td>
<td>46,3</td>
</tr>
<tr>
<td>4</td>
<td>0,8868</td>
<td>−1°22'</td>
<td>88,0</td>
<td>33,5</td>
<td>38,8</td>
<td>39,5</td>
</tr>
<tr>
<td>5</td>
<td>0,8883</td>
<td>−1°28'</td>
<td>87,5</td>
<td>40,1</td>
<td>38,7</td>
<td>35,4</td>
</tr>
<tr>
<td>6</td>
<td>0,8925</td>
<td>−2°11'</td>
<td>84,7</td>
<td>35,9</td>
<td>38,0</td>
<td>37,2</td>
</tr>
<tr>
<td>7</td>
<td>0,8881</td>
<td>−1°11'</td>
<td>91,0</td>
<td>37,0</td>
<td>36,8</td>
<td>40,1</td>
</tr>
</tbody>
</table>

*JAVA OILS.*

<table>
<thead>
<tr>
<th>Nr.</th>
<th>d₁₅₀</th>
<th>α₀</th>
<th>So-called total geraniol (est. by acet.)</th>
<th>Geraniol (phthalic anhydride method)</th>
<th>Citronellal Phenyl-hydrazine method (Kleber)</th>
<th>Oximation method (Dupont and Labaune)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0,9012</td>
<td>−11°22'</td>
<td>54,1 p.c.</td>
<td>30,7 p.c.</td>
<td>11,4 p.c.</td>
<td>7,9 p.c.</td>
</tr>
<tr>
<td>2</td>
<td>0,9016</td>
<td>−11°28'</td>
<td>57,2</td>
<td>33,2</td>
<td>11,0</td>
<td>8,0</td>
</tr>
<tr>
<td>3</td>
<td>0,9034</td>
<td>−11°40'</td>
<td>58,6</td>
<td>30,0</td>
<td>11,6</td>
<td>7,8</td>
</tr>
<tr>
<td>4</td>
<td>0,9039</td>
<td>−11°43'</td>
<td>56,3</td>
<td>29,8</td>
<td>10,8</td>
<td>6,7</td>
</tr>
<tr>
<td>5</td>
<td>0,9033</td>
<td>−11°31'</td>
<td>57,6</td>
<td>30,8</td>
<td>11,5</td>
<td>7,9</td>
</tr>
</tbody>
</table>

*CEYLON OILS.*

Taking into account at the same time the values previously obtained by us¹) we find in the case of Java citronella oil a geraniol content of 26,6 to 40,1 p.c. and a citronellal content of 35 to 41,3 p.c. (phenylhydrazine method) or 35,4 to 46,3 p.c.

¹) *Report* October 1899, 18; April 1900, 13; October 1912, 42.
(oximation method). For Ceylon oil we have so far found from 29.6 to 34.4 p. c.
geranion, and, according to the method employed from 7.5 and 11.6 (Kleber) or 6.5 and
8.0 p. c. (Dupont and Labanne) citronellal.

It has been shown that for the phenylhydrazine method it is advisable to take
1 gram Ceylon oil or 0.5 gram Java oil (exactly weighed), for the rest the method is
applied as described in our Report of April 1912, p. 75, for lemon oil. The phenyl-
hydrazine must be allowed to react for at least one hour and the reaction may be
prolonged to 1 1/2 hours, but it is not advisable to let it proceed beyond that limit,
because then the phenylhydrazine solution acquires such an intense colour as to
make titration more difficult.

As regards the special estimation of geranion by means of phthalic anhydride, it
goes without saying that in this case the other primary alcohols which occur in citro-
nella oil (nerol and citronellol) also enter into reaction, but they are quantitatively of
so little importance that there is no need to pay any attention to them in carrying out
the estimation.

In connection with the above we may mention that we have also tested the phenyl-
hydrazine method with a series of other aldehydes and ketones. These tests showed
that cuminic aldehyde, benzaldehyde, and methylnonylketone may be quantitatively
estimated by the same method, while fenchone, thujone, camphor, and menthone give
no reaction at all with phenylhydrazine. In each case the quantity used for estimating
was from 0.12 to 0.15 grams. The following table gives particulars of the results
obtained:

Cuminic aldehyde (cont. 2.7 p. c. cuminic acid) found 95.7 and 96.2 p. c. cuminic aldehyde,
50 p. c. cuminic aldehyde + 50 p. c. carvene 1)  found 51.5 and 49.5 p. c. cuminic aldehyde,
Benzaldehyde (cont. 2.4 p. c. benzoic acid) . found 98.0 and 99.6 p. c. benzaldehyde,
Methylnonylketone . . . . . . . . . . . . . . . . . found 99.7 and 98.6 p. c. methylnonylketone.

It should be borne in mind that cuminic aldehyde and benzaldehyde may contain
free acid due to oxidation. This explains why otherwise pure aldehydes in certain
circumstances did not afford 100 p. c. By this method we found cumin oils to contain
between 35 and 42 p. c. of cuminic aldehyde. In the case of bitter almond oils con-
taining hydrocyanic acid (as more fully explained on p. 24 of the present Report), only
the free benzaldehyde and not that which is in combination with hydrocyanic acid,
enters into reaction with phenylhydrazine.

As we have shown, methylnonylketone is also capable of being estimated quanti-
tatively, and the same probably applies to the methylheptylketone which has been
detected in oil of rue; hence the method may eventually be used for testing the last-
named oil. Here, however, it should be remembered that in rue oil both the ketones
are always present in varying proportions. Hence the quantity of phenylhydrazine
which has been used only affords an approximate clue to the quantity of the ketones,
and it must at the same time be ascertained, by determining the solidifying-point,
which of the two ketones predominates in the oil, and whether it will be more practic-
cable in estimating to use as a basis the molecular weight of methylnonylketone (170)
or that of methylheptylketone (142). It remains to be seen to what extent this will
afford practically useful results. We found the value for an oil of rue with about

1) The carvene used by us as a diluent had been repeatedly distilled over sodium, but nevertheless it
used up a quantity of phenylhydrazine corresponding to a proportion of from 0.4 to 0.6 p. c. cuminic aldehyde.
9° sol. pt. according to the phenylhydrazine method, to be 100 p. c. calc. for methyl-
nonylketone. In reality this value was of course too high, owing to the presence in
the oil of methylheptylketone as well as methylnonylketone.

From the analysis of a citronella oil sample recently submitted to us, we believe
ourselves to be justified in concluding that certain kinds of motor-spirit (automobile-
benzine) have lately been used as adulterants of Ceylon citronella oil. The sample in
question showed the following constants:  d₄₀ 0,8873,  ε₉₂ — 11° 12', so-called total
geraniol 55,6 p. c.; sol. in its own vol. of 80 p. c. alcohol; upon the addition of 5 vols.
of the solvent the solution becomes almost turbid. The sample barely answered
Schimmel's test, and failed to answer Schimmel's "raised test."

Although the percentage of so-called total geraniol must be described as tolerably
sufficient, the oil is obviously suspect on account of its sp. gr., which is much too
low, and because it is doubtful whether it can or cannot be said to answer Schimmel's
solubility test. When the sample was subjected to further examination, it was found
that this abnormality was, clearly due to sophistication, and that the oil contained
about 10 p. c. of a fraction boiling between 80 and 160°, whereas a check test shewed
that of a sample of normal oil practically nothing at all passed over below 160°.

Unfortunately, the sample sent to us was insufficient for a thorough examination
of the fraction in question; but it would appear that it consisted of low-boiling petroleum
hydrocarbons. This suspicion was confirmed because experiments showed that it is
quite possible for a citronella oil of good quality still to answer the solubility-test
after an addition of 10 p. c. or even more of benzine. But apart from this the adulteration
could not have escaped the notice of a careful observer, insomuch as it can be imme-
diately detected (as was also the case with the sample in question), from the reduced
sp. gr.; a constant which in normal Ceylon citronella oil ranges from 0,900 to 0,920.
It will therefore be advisable in future examinations to take special notice of this
constant, but in addition to this we would again call attention to our "raised test"
(testing the solubility of a sample after adding 5 p. c. petroleum), as this test would
in most cases, we think, reveal adulterations of the character described. Presumably
the method recommended by Dodge¹), consisting of oxidation with potassium permanganate,
would also be serviceable in detecting an addition of the above nature. In
applying this test the adulterant, which consists entirely of hydrocarbons, would remain
unattacked.

We hope to be able to give further particulars on this subject as soon as we
have examined a larger quantity of oil sophisticated in this manner.

On the detection of petroleum in citronella oil see p. 129.

On a Burmese citronella oil see p. 71.

Clove Oil. Since the publication of our last Report the prices of clove oil have
been repeatedly advanced, and it appears to us that the end of the upward movement
has not yet been reached. Events have shown that our estimate of the yield of the
summer crop was still too high, and it is now certain that the winter-crop also has
not yielded more than 30 000, or at the most 40 000 bales, while the world's annual
requirements of cloves amount to 120 000 bales. It is therefore not surprising that the

¹) Comp. p. 62 of the present Report.
prices of cloves have considerably advanced. For the time being the position of the market is firm, but in spite of this there have been several opportunities of laying in supplies at advantageous prices below the current value, because the stringent condition of the money market has induced a number of speculators to realise hurriedly. Of course, no one can say what will be the further development of the market, but rumour has it that the crop of the coming summer is likely to be very heavy. It is, in fact, not unreasonable to expect an improvement in the yield of the crop after two successive failures.

Unfortunately neither German nor foreign Consular Reports on the trade of Zanzibar have been published for a long time, and as these reports usually contain statistical data on the production of cloves, we are for the present unable to bring the figures (of which the last relate to the year 1910) up to date. We cannot account for the absence of the Consular Reports in question.

From a report of the German Consulate at Amsterdam we gather that the aggregate sales of cloves at Amsterdam and Rotterdam in 1912 amounted to 48,700 bales, as compared with 16,600 and 42,100 bales in the years 1911 and 1910 respectively.

The stocks of both descriptions (Zanzibar and Amboyna) at Amsterdam in December amounted to 540 tons, which compared with 407 and 744 tons respectively in the two previous years.

The highest and lowest prices are given as follows:—

<table>
<thead>
<tr>
<th>Year</th>
<th>Amboyna Cloves</th>
<th>Zanzibar Cloves</th>
</tr>
</thead>
<tbody>
<tr>
<td>1908</td>
<td>50 and 42 Cents</td>
<td>29 and 23 Cents</td>
</tr>
<tr>
<td>1909</td>
<td>43 &quot; 37 &quot;</td>
<td>29 &quot; 23 3/4 &quot;</td>
</tr>
<tr>
<td>1910</td>
<td>52 &quot; 42 &quot;</td>
<td>39 3/4 &quot; 25 7/8</td>
</tr>
<tr>
<td>1911</td>
<td>50 &quot; 46 &quot;</td>
<td>43 1/2 &quot; 27 3/4</td>
</tr>
<tr>
<td>1912</td>
<td>53 &quot; 43 &quot;</td>
<td>54 1/4 &quot; 28 &quot;</td>
</tr>
</tbody>
</table>

H. Klein, in an interesting article on Indian usurers at Zanzibar 1), describes the desperate condition of the Arab clove-planters in the island, and the nefarious practices of the Indian money-lenders there. We quote the following passages from the article:—

“As soon as the Arab has sold his cloves, the produce of his plantation, he lives riotously on the fat of the land until the cash is gone. Then, as he is generally without the means even of doing the most urgent weeding and cleaning on his plantation so that the crop may at least be more or less saved, there is nothing left for him but to pay a visit to the money-lender, the Indian. When the crop is ripe the Arab again needs cash to pay his labourers' wages. Some of them sell their crop a year before it is ripe, at a price which does not even cover the cost of gathering. And so the borrowing goes on, year in year out. When the Indian thinks that he has lent his debtor enough money he begins to tighten the noose; may be he allows the planter a short breathing space, just to show that even a money-lender has a soft side, but the end is inevitable: the plantation comes under the hammer. It may be taken for a fact that more than half of the Arab plantation-owners have recourse to the usurer to find the wherewithal, and it goes without saying that every man of them finally falls a victim to the Indian money-lender.

Sales by Order of Court of clove- and cocoanut-plantations owned by Arabs are of daily occurrence in Zanzibar. It is only a matter for regret that the gardens

1) *Homb. Fremdenblatt* 1913, No. 63.
are usually sold at knock-out prices. I have attended auctions where the offers represented less than one rupee for every clove-tree on the plantation, and where the lot was bought in because no high enough bid could be obtained. It is a matter for astonishment that up to the present no European has taken the chance offered by such bargains as are going in plantations: it would be impossible to become possessed of a clove-garden more quickly or more cheaply than here.

In all money-lending transactions regard must be had to the rate of interest which is charged. No one in Zanzibar thinks it amiss to ask 30 p. c. interest. But the average rate of interest is very much higher than that; some of these leeches are not ashamed to squeeze 300 p. c. out of their victims. These money-lenders resort to all manner of tricks to get their usury-rates. The most common practice is as follows: — The Arab borrows 100 Rupees from the Indian; but the money-lender makes him sign a bond for 1500 Rupees or even more, and when the time of payment comes interest to a not inconsiderable amount is charged on the amount stated in the bond in addition to the principal. The best laws and regulations are powerless against such sharp practice; yet nowhere is an energetic campaign against usury more urgently needed than in Zanzibar. So far as is known, the Government regards a rate of interest of up to 12 p. c. as lawful. But the Indian does not trouble himself about that. No debtor dares to make known to the authorities what interest he has undertaken to pay; if he did he would be digging his own grave, so to speak, for never another copper would the Indian usurer-fraternity lend him. About six years ago the Government established a so-called Agricultural Bank, where the Arabs can obtain advances on their crops at a low rate of interest. This was done expressly to get them out of the clutches of the Indian usurers, but the Bank has been altogether unsuccessful.

It would truly be a difficult task to clean out this welter of usury in Zanzibar, for although the business is chiefly conducted by Indians, other races, including Europeans, also take a hand in it. Usury appears to have entered into the very bones of the whole population, and nothing but severe measures, which would at first be felt as a hardship, could in the course of time bring about an improvement. If the economic life of Zanzibar is to be restored to healthy conditions, the Government must make it its business to clear out this system of usury that has made such an unprecedented growth within the last decades, and that forms a grave danger to the economic development of the country. If the Government should succeed, the production of the country would again expand, the revenues of the Sultanate would increase, and the entire economic life of Zanzibar would be restored to health. But for the present all this is in the dim and distant future, for the British Government of Zanzibar is not likely to be easily persuaded to adopt such stringent measures."

From a report by the British Consul at Antananarivo¹ it appears that the clove-plantations in the island of Madagasca number 400000 trees, of which 230000 are on the island of Ste-Marie. In that island the clove-plantations cover an area of 2391 acres, of which 415 have been laid down by Europeans and the rest by natives. The exports of cloves during the year 1911 amounted to 288237 lbs., of the value of £ 10000.

According to A. Chevalier² the clove-tree is now fairly widely distributed throughout the French Congo, although there is no question of any cultivation of cloves in

¹ Pharmaceutical Journ. 89 (1912), 571. — ² Compt. rend. 155 (1912), 1091.
that colony. Until 25 years ago the tree was quite unknown in this region. The first plantations were laid down in 1887, and in 1893 the trees flowered for the first time. A ten-year-old tree is able to produce from 5 to 10 kilos of cloves.

**Cocoa Oil, essential.** It was formerly assumed that the aromatic substance in cocoa (from *Theobroma Cacao, L. N. O. Sterculiaceae*) was identical with, or associated with, cocoa-red. This assumption however, is quite erroneous; in fact, cocoa-red is an odourless body, and the distinctive aroma of cocoa is due to the presence of an essential oil. This volatile oil has been more closely examined by J. S. Bainbridge and S. H. Davies 1). These investigators distilled 2000 kilos cocoa-nibs, which yielded 24 grams (≈ 0,001 p. c.) oil, consisting of (I) the essential oil which was originally present in the cocoa-nibs and (II) of a body which was probably formed only in the fermentation-liquid of the nibs and which had been absorbed therefrom by them. The latter body consisted almost wholly of the esters of the lower fatty acids. The constants of the total oil were as follow: \( d_{15} \) 0,9075, \( n_{D20} \) 1,4728. It contained the following free acids: valeric acid (combustion); a mixture of caprylic and \( n \)-caprinic acid (analysis of the silver-salt of the acid mixture) and perhaps caproic acid. Traces of a nitrogenous compound with a disagreeable odour were separated out from the oil by washing with sulphuric acid. The oil contained no primary alcohols: the calcium chloride which had been used for drying had not combined with alcohols. The only esters found present were amyl acetate, amyl propionate, and amyl butyrate, with possibly, hexyl butyrate and \(-\)-propionate. The authors consider that the principal constituent (over 50 p. c.) of the oil which is originally present in the nibs consists of \( \delta \)-linalool (b. p. 87 to 97\(^\circ\) [15 to 11 mm.]; \( d_{15} \) 0,8936; [\( \alpha \)]\(_{D20}\) +11° 36; \( n_{D20} \) 1,4658). The phenylurethane melted between 60 and 61\(^\circ\).

**Coffee oil.** We have already on a previous occasion 2) reported on the aromatic substances found in roasted coffee-beans; the so-called caffeol (coffee oil or caffeione). Since that time, V. Grafe 3) has carried on investigations into the origin of the furfur alcohol which is present in coffee oil, and which, with valeric acid, acetic acid, and a nitrogenous aromatic substance, constitutes 50 p. c. of the coffee oil. Grafe concludes that the furfur alcohol originates from the crude fibres of the coffee-beans, probably mostly from the hemicellulose of the thickened endosperm cells. The fact that furane-derivatives can be prepared in considerable proportions and without trouble from cellulose is in accord with the derivation of furfur alcohol from the crude fibres.

**Coriander Oil.** According to information received from our correspondents, the coriander crop in Russia has amounted to about 10000 poods of a barely average quality, and the greater portion of this has already passed into the control of firm holders. When the large stocks of 1911, which had accumulated owing to the sluggish demand, were used up, the coriander prices gradually advanced. We have been compelled to follow the market and in view of the lengthy period which has still to elapse before the new crop is available we see no chance of a backward movement in values.

**Cumin Oil.** Some time ago 4) a parcel of cumin seed from Persia was offered for sale on the London market. Upon distillation the seed yielded 2 p. c. of an oil

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possessing the following constants: $d 0.911, a_B + 7^\circ, n 1.4980$. The oil contained 18 p.c. of aldehydes (by the bisulphite method) and its odour was sweeter than that of ordinary cumin oil. It did not appear to contain carvone. According to Holmes\(^1\), Persian cumin seed is known in Bombay as Zeerah Siah, the ordinary seed from *Cuminum Cyminum* being there known as Zeerah Suffed. The Persian fruit is probably derived from *Carum gracile*, Lindl. (*C. nigrum*, Royle), of which Holmes gives an illustration taken from a herbarium-specimen in the Botanical Museum of Cambridge. The seed is also mentioned in Dymock's *Materia Medica of Western India* (Bombay and London, 1885, p. 368) by the name of Sajire or Siah-zirah.

Among the few umbellifers of which the fruit has an odour of cumin is also *Psammogeton setifolium*, Boiss., but its fruit differs clearly from both the Persian and the ordinary cumin, hence this species cannot be regarded as the parent plant of the seed in question.

Sage\(^2\) has studied the anatomical characters of the fruit of both varieties of cumin. He publishes accurate illustrations both of the entire fruit and of the transverse sections, which enable the drug to be clearly distinguished.

For the quantitative estimation of cuminic aldehyde, comp. p. 45.

**Oil of Cydnus indicus.** According to E. R. Watson\(^3\) an evil-smelling Indian bug (*Cydnus indicus*) exudes a fatty oil which contains about 1.5 p.c. of constituents volatile with steam. These constituents are composed of an acid $C_8H_{14}O_2$, probably cycloheptane carboxylic acid, and a small quantity of a non-acid compound which may possess the empirical formula $C_{11}H_{20}O_4$. The acid has a strong rancid odour; that of the non-acid substance is more powerful still.

**Cypress Oil.** This well-established whooping-cough remedy is being increasingly appreciated among the medical faculty, both in Germany and abroad, hence the demand has been very brisk indeed, especially during the cold months. We have been able to replenish our stock in good time from our works at Barrême, in France, where we are able to distil exquisite raw material in a quite fresh condition. Owing to the particularly favourable conditions under which our manufacture is conducted, we have lately been able to reduce our prices somewhat, but we specially warn our readers against cypress oils which are being offered too cheaply, as the origin of these is very doubtful, and they are generally without any medicinal virtue whatever. We shall be glad to send printed matter upon application for distribution among medical practitioners.

In the year 1904\(^4\), when we published the results of our examination of cypress oil, we referred incidentally to two alcohols, one of which at the time we thought ourselves warranted in describing as sabinol. Recently we have again taken up this research, with the result that we discovered the principal constituent of the alcohol-mixture (distilled between 70 and 85\(^\circ\), 3 to 4 mm.) to be an alcohol $C_{16}H_{30}O$, = terpinenol-4, a body of which we had previously detected the presence in European wormseed oil\(^5\), juniper-berry oil\(^6\) and nutmeg oil\(^7\). The mixture was treated with pyridine and benzoylchloride for the purpose of removing the esterifiable alcohols contained in it. The

whole of the non-esterifiable oil was driven off with steam from the benzoic ester which had been generated and split up by distillation into the two fractions referred to below, which were used for the detection of the terpinenol by the direct method.

1. B. p. 66 to 69° (3 mm.), 212 to 214°, $d_{15}$ 0,9410, $\alpha_D + 25° 0'$, $n_{D20} 1,48354$.
2. B. p. 69 to 71° (3 mm.), 214 to 225°, $d_{15}$ 0,9445, $\alpha_D + 29° 30'$, $n_{D20} 1,48461$.

Fraction I was oxidised with 1 p.c. permanganate solution with ice-cooling and stirring. From the evaporated residue of steam-distillation we extracted (with chloroform) a glycerol which crystallised when stirred with water in the cold. When repeatedly purified from chloroform this body melted, not very sharply, between 111 and 114°, and when carefully heated it sublimed in lustrous crystals melting sharply at 129°. When distilled with dilute hydrochloric acid it gave rise to cymene and to a ketone with an unmistakable odour of carvenone. M. p. of the semicarbazone about 200°. By oxidising with permanganate in the presence of alkali the glycerol was converted into $\alpha,\alpha'$-dihydroxy-$\alpha$-methyl-$\alpha'$-isopropyladipic acid (m. p. 191 to 198°). The want of sharpness in the m. p. is explained by the assumption that the body constitutes a mixture of the active acid, m. p. 205 to 206° with the inactive, m. p. 188 to 189°. Boiling with dilute acid converted it into a lactone, m. p. 68 to 71°, volatile with steam. Here also a mixture may be assumed to exist of the two dilactones (m. p. respectively 63 to 64° and 72 to 73°) which are derived from the above-named acids. Owing to the exceedingly small quantity available, both of the acid and of the lactone, separation of the two isomerides was out of the question. Finally we were able to resolve the dihydroxy acid into $\omega$-dimethylacetonyl acetone by oxidising it with permanganate in acid solution. The m. p. of the semicarbazone was about 200°.

The second alcohol-fraction mentioned above only yielded a very small proportion of solid glycerol when oxidised. This fact, together with the different behaviour of the glycerol mother-liquors during oxidation, makes it probable that this fraction was no uniform product and that it only contained very little terpinenol-4. No further characteristic resolution-products were obtainable. Owing to lack of material it was impossible further to investigate the question whether sabinol was actually present in fraction 2.

With regard to the other alcohol of which we made mention in our Report of April 1904, we have been able to obtain the following further particulars: It is esterifiable with benzoyl chloride (using pyridine) and was recovered from the steam-distillation residue by saponification. For purposes of purification it was again treated with phthalic anhydride at an increased temperature. Unfortunately, in this manipulation part of it was decomposed. The pure alcohol $C_{10}H_{18}O$ has a pleasant, rose-like odour, reminding at the same time of borneol. Its constants were as follow: b. p. 76 to 77° (4 to 5 mm.), 210 to 212° (ordinary press.), $d_{15}$ 0,9422, $\alpha_D + 43° 38'$, $n_{D20} 1,46678$.

$0,1364$ gr. Sbst.: 0,3910 gr. CO$_2$, 0,1425 gr. H$_2$O.

<table>
<thead>
<tr>
<th></th>
<th>Calc.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>77,92%</td>
<td>78,10%</td>
</tr>
<tr>
<td>H</td>
<td>10,67%</td>
<td>11,65%</td>
</tr>
</tbody>
</table>

With phenyl and naphthylisocyanate only liquid derivatives were obtained. No diphenylurethane was formed. Judging by the odour, oxidation with Beckmann’s mixture appears to give rise to an aldehyde.

With regard to the cypress oil fractions with the highest b. p., which possess in a more pronounced degree the peculiar balsamic odour, it would appear from our most recent observations that they contain, besides cadinene and cypress-camphor, a
second, liquid, sesquiterpene alcohol. This alcohol boils between 136 and 138° (4 to 5 mm.) that is to say at a considerable higher degree than does cypress-
camphor, which was the principal body found in the fractions with b. p. 123 to 125°
(4 mm.). When warmed with strong formic acid, the alcohol is converted into a
hydrocarbon, water being eliminated. Combustion confirmed the body to be an
alcohol with the formula \( \text{C}_{15}\text{H}_{28}\text{O} \).

\[
0.1759 \, \text{gr. Sbst.: } 0.5247 \, \text{gr. CO}_2, 0.1842 \, \text{gr. H}_2\text{O.}
\]

Calc. for \( \text{C}_{15}\text{H}_{28}\text{O} \) Found

\[
\begin{align*}
\text{C} & \quad 81.82\% \quad 81.35\%\\
\text{H} & \quad 11.71\% \quad 11.64\%
\end{align*}
\]

So far we have been unable to identify it from any derivatives.

**Oil of Erysimum Perofskianum.** A homologue of the sulphone mustard oil
theirolin\(^1\) which can be isolated from wallflower seed, has been obtained from the
seed of *Erysimum Perofskianum*, Fisch. et Mey. (N. O. Cruciferae), by W. Schneider,
working in collaboration with H. Kaufmann\(^2\). Its empirical formula is \( \text{C}_8\text{H}_{11}\text{O}_2\text{NS}_2 \) (that
of theirolin being \( \text{C}_5\text{H}_9\text{O}_2\text{NS}_2 \)), and it is called erysolin from its origin. The yield from
1 kilo of green seed, containing fatty constituents, was at most 0.5 gram. (= 0.05 p. c.).
Recrystallised from ether, erysolin forms beautiful, colourless prisms (m. p. 59 to 60°)
which strongly excite the mucous membrane. With alcoholic ammonia it yields a
sulpho-urea, melting between 143 and 144°. Saponification with hydrochloric acid led
to the base of erysolin from which, by oxidation with nitric acid, \( \gamma \)-aminobutyl-methyl-
sulphone was obtained. Owing to the scarcity of available material it was impossible
to carry the resolution further. It was, however, found possible to prepare erysolin
synthetically. With this object in view, chlorobutynitrile was allowed to react with
the calculated quantity of sodium mercaptide, when \( \gamma \)-methyl sulphide butyronitrile,
\( \text{CH}_3\cdot\text{S} \cdot (\text{CH}_2)_3 \cdot \text{CN} \) was formed. The latter, when reduced with sodium and alcohol
yielded \( \delta \)-aminobutyl methylsulphide \( \text{CH}_3\cdot\text{S} \cdot (\text{CH}_2)_4 \cdot \text{NH}_2 \), of which the dilute aqueous
solution has an odour reminding of that of crab or lobster. When oxidised in acetone
solution with hydrogen peroxide this sulphide yields \( \delta \)-aminobutyl methyl sulphoxide
(\( \text{CH}_3\cdot\text{SO} \cdot (\text{CH}_2)_4 \cdot \text{NH}_2 \)), from which, upon oxidation with potassium permanganate in
acid solution, \( \delta \)-aminobutyl methylsulphone (\( \text{CH}_3\cdot\text{SO}_2 \cdot (\text{CH}_2)_4 \cdot \text{NH}_2 \)) resulted. The latter,
in alcoholic solution with carbon disulphide, was converted into the dithiocarbamine
(II)\(^3\) which, in its turn, was oxidised with iodine into the corresponding dithiurame

\[
\begin{align*}
\text{CH}_3\cdot\text{SO}_2 \cdot (\text{CH}_2)_4 \cdot \text{NH} & \quad \rightarrow \quad \text{CH}_3\cdot\text{SO}_2 \cdot (\text{CH}_2)_4 \cdot \text{NH} \\
\text{CH}_3\cdot\text{SO}_2 \cdot (\text{CH}_2)_4 \cdot \text{NH}_2 \cdot \text{HS} & \quad \rightarrow \quad \text{CH}_3\cdot\text{SO}_2 \cdot (\text{CH}_2)_4 \cdot \text{NH}_2 \\
\text{CH}_3\cdot\text{SO}_2 \cdot (\text{CH}_2)_4 \cdot \text{N} \cdot \text{S} \cdot \text{C} \cdot \text{S} \cdot \text{Na} & \quad \rightarrow \quad \text{CH}_3\cdot\text{SO}_2 \cdot (\text{CH}_2)_4 \cdot \text{N} \cdot \text{S} \cdot \text{C} \cdot \text{S} \cdot \text{Na}
\end{align*}
\]

\( \text{I (Dithiocarbamate).} \quad \text{II (Dithiurame disulphide).} \quad \text{III (Na-salt of dithiurame disulphide).} \quad \text{IV (\( \delta \)-Thiocarbimidobutyl-methylsulphone).} \)

\(^1\) Comp. Report October 1910, 85. \(^2\) Liebig's Annalen 392 (1912), 1. \(^3\) By J. v. Braun's method,
Ber. Berichte 45 (1912), 2188; Report October 1912, 164.
disulphide (II). The sodium salt of this compound (III) was next decomposed with iodine, whereupon the desired mustard oil, $\delta$-thiocarbimido butylmethylsulphone (IV) was isolated in satisfactory proportions from the reaction-liquors. The synthetic mustard oil proved to be completely identical with erysolin. A mixture of the two bodies produced no depression of melting-point. The $\delta$-aminobutyl methylsulphone from the synthetic product was likewise identical with that obtained from natural erysolin.

Essential Oils, Sicilian and Calabrian.

Mr. Eduardo Jacob, of Messina, in his usual obliging manner, has furnished us with a report on these important articles, which we reproduce verbatim below:

In the year 1912 the exports have exceeded those of the previous year by 61,972 Kilos and by 4,725 lire, that is to say, there has been an excess of about 8 p.c. in weight and of about 30 p.c. in value. The increase in value is due for the smaller part to the fact that the prices of lemon oil have been continually rising throughout the year, but chiefly to the great increase in the value of bergamot oil, which in the months of January and February of the year under review rose within a few weeks from 45 $\mathcal{M}$ to 67 $\mathcal{M}$ and of which the average value throughout the year was maintained at about 55 $\mathcal{M}$. This high range of values has, generally speaking, been caused by the reduced crops of the winter 1911/1912. All varieties of essences have been firmly held throughout the year, because the available stocks were barely sufficient to meet the consumption, and the owners were therefore in a position to maintain their pretensions. It is true that in the face of these high prices the consumption has been restricted as far as possible, but in spite of this the stocks of all oils available in the warehouses here have been gradually used up, and therefore, as soon as the new oil of the 1912/1913 crop made its appearance, it encountered a market in which the need of supplies was felt to an extraordinary degree.

No deviations from the normal have been observed in the physico-chemical constants of the present season's essences unless it be that bergamot oil shows a rather lighter specific gravity and lemon oil a somewhat lower rotation than the oils of last year.

Passing to the particular varieties of essential oils, I have to report as follows:

Bergamot Oil. In September of last year the approximate price of this oil was 55 $\mathcal{M}$. Notwithstanding that the consumption of bergamot oil has been very seriously affected by the presence of so many cheap substitutes, the demand has been so strong that the available supplies were quite used up as early as the commencement of November; hence the new oil, which on this occasion reached the market a little earlier than in the two previous seasons, immediately found ready buyers.

In the course of the autumn-months sales of this oil had been made for delivery to foreign countries at an average price of from 52 $\mathcal{M}$ to 53 $\mathcal{M}$, and speculators who thought themselves clever had already discounted the knowledge that the crop was rather better than that of the previous season, by making bear-sales at from 45 $\mathcal{M}$ to 50 $\mathcal{M}$. The depletion of the stocks of old oil, however, before the arrival on the market of the new, and the sustained foreign demand, which received the new crop with open arms, so to speak, naturally caused an immediate rise in the value of the new oil for which, consequently, as early as the beginning of December, from 55 $\mathcal{M}$ to 56 $\mathcal{M}$ had to be paid.
Exports of Essential Oils in the year 1912.

<table>
<thead>
<tr>
<th>Country of Destination</th>
<th>1911 Kilos</th>
<th>1911 Lire</th>
<th>1912 Kilos</th>
<th>1912 Lire</th>
</tr>
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<tr>
<td>a) Messina:</td>
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</tr>
<tr>
<td>North German Ports</td>
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<td><strong>Total</strong></td>
<td>457,712</td>
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<td>617,693</td>
<td>14,824,632</td>
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b) Catania:

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<tr>
<th>Country of Destination</th>
<th>1911 Kilos</th>
<th>1911 Lire</th>
<th>1912 Kilos</th>
<th>1912 Lire</th>
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<td>90,555</td>
<td>2,173,320</td>
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Commercial notes and scientific information.

<table>
<thead>
<tr>
<th>Country of Destination</th>
<th>1911 Kilos</th>
<th>1911 Lire</th>
<th>1912 Kilos</th>
<th>1912 Lire</th>
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d) Palermo:

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<th>1911 Lire</th>
<th>1912 Kilos</th>
<th>1912 Lire</th>
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<tr>
<td>North German Ports</td>
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<td>Italy</td>
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<td></td>
</tr>
<tr>
<td>Other countries</td>
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</tr>
<tr>
<td>Total</td>
<td>114,035</td>
<td>2,280,700</td>
<td>55,400</td>
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Total Exports in 1912:

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<th>1911 Kilos</th>
<th>1911 Lire</th>
<th>1912 Kilos</th>
<th>1912 Lire</th>
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<td></td>
<td></td>
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<tr>
<td>Messina</td>
<td>457,712</td>
<td>9,154,240</td>
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<td>14,824,632</td>
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<td>Catania</td>
<td>129,141</td>
<td>2,582,820</td>
<td>90,555</td>
<td>2,173,320</td>
</tr>
<tr>
<td>Reggio (Calabria)</td>
<td>66,483</td>
<td>1,662,075</td>
<td>65,695</td>
<td>2,299,325</td>
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<tr>
<td>Palermo</td>
<td>114,035</td>
<td>2,280,700</td>
<td>55,400</td>
<td>1,108,000</td>
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<tr>
<td>Total</td>
<td>767,371</td>
<td>15,679,835</td>
<td>829,343</td>
<td>20,405,277</td>
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1912 Kilos: 829,343 Lire: 20,405,277
1911 Kilos: 767,371 Lire: 15,679,835

1912 increase Kilos: 61,972 Lire: 4,725,442

+ about 8 p.c. by weight. + about 30 p.c. by value.
Fortunately the working up of the new fruit proceeded under normal conditions. The state of the weather favoured the preparation of oil, and although the oil-yield of the fruit was not abundant, the results have generally been satisfactory. If notwithstanding all this prices began to rise slowly in the course of December and reached the parity of 60 1/2 in the first half of January, the reason must be sought on the one hand in the strong demand from abroad, especially from France, and on the other in the circumstance that the Sicilian manufacturers, by keeping back their merchandise for some weeks, contrived to provoke a pronounced scarcity, and thus succeeded in compelling a few exporters who had entered into contracts for delivery, to concede the increased demands of the holders.

But this artificial and unnatural condition of high prices could not be maintained long, and from the end of January onwards the quotations for bergamot oil began to sag slowly. Since then the tendency has been slowly drooping, and gradually a price-level of 53 1/2 was reached.

The future of the article will be determined mainly by the prospects of the coming crop. The stocks which are held in the producing country are amply sufficient to meet the normal requirements of the world, and to preclude any scarcity of material in the course of the present season.

The foliage of the trees is splendid, and their appearance would justify the highest expectations were it not that the flowering has already proceeded a little too far for the time of the year. In such a precocious development so early in the season present and future dangers lie hidden which may easily spell disaster for the coming crop. If the bergamot trees should escape those climatic influences which may threaten the flower and the young fruit until far into the summer, the likelihood of the prices of bergamot oil undergoing a reduction would increase in proportion as the time of the next gathering draws nearer.

**Lemon Oil.** The business in lemon oil has passed through a time of exceptional difficulty last year and during the first quarter of 1913. During that period a number of various unfavourable factors, the like of which has probably never before operated at one and the same time, has exercised a pernicious influence upon the trade in this article.

In order to make these circumstances clear it is necessary to revert to the statistical position of lemon oil at the commencement of the year 1912. Whereas in the winter of 1910 to 1911 a balance of over 100,000 kilos of old oil was carried over into the new season, only about 30,000 kilos of such lemon oil remained in December 1911 to augment the new crop of 1911/12. In the course of the year 1912 the consumption not only swallowed up the whole 30,000 kilos of old stock, but in addition thereto the entire output of the winter-season of 1911/1912; hence the new crop of the season 1912/1913 was called upon to fulfil the requirements of an entirely depleted market. For the year 1913 therefore, the consumption has nothing to fall back on except the produce of the manufacturing-season of 1912/1913.

In these circumstances it would have been of the utmost importance for every dealer in the article to be in a position to form an accurate judgment of the new crop while it was still on the trees. Whenever an article is left to itself, that is to say, when it is affected solely by the law of supply and demand, it is not very difficult, given a little experience, to form an opinion of its commercial position. But when, either in the country of production or in the consuming markets, powerful groups of speculators are formed, who by artificially raising or depressing the prices of the
commodity in question make it difficult to obtain a survey of its true position, such a strained state of affairs usually ends in a catastrophe, because only a minority of the speculators are capable of forming any correct judgment of the article at all, and the majority, like a flock of sheep, blindly follow the bell-wether. During the last few years a large firm in Messina had played the part of bell-wether to the speculative herd of operators in the oil market, and fortune appeared to smile upon its undertakings. At any rate it is certain that within the last three years those speculators which followed the firm in question made very fine profits, and that their good fortune caused the herd to grow larger year by year, for everybody was anxious to secure his share of the golden bounty that could be had so easily and with so little trouble. It cannot be explained in what manner this firm, previously so intelligently conducted, came to misapprehend the difficult statistical situation of lemon oil, and thereby to lead the colossal local speculative movement in Messina into the wrong lines, but this much is certain, that the export-firm in question, together with the majority of local speculators, has entered upon bear-operations of great magnitude.

We have therefore witnessed a repetition of the usual occurrence, namely, that with small supplies of old oil, scarcely sufficient to carry the trade forward to the new season, and with relatively good crop-prospects, a few Messina export-houses made large uncovered sales at low prices both for export and to dealers on the local market. A large number of manufacturers and local speculators associated themselves with this movement, until in the end the Messina market had entered into engagements which exceeded in amount the whole of the new season's oil-output. And when, in the course of the summer, owing to unfavourable climatic conditions, the prospects of the new crop grew worse and worse, both old oil and new oil for delivery rapidly advanced to a high level of prices.

Old lemon oil rushed upwards from 13 \( \times \) in June to 17,50 \( \times \) at the beginning of September; new oil for delivery rose from 12 \( \times \) in June to 16 \( \times \) in the first days of September. When the supplies of old oil were practically cleared, the bear-party in Messina made another strong effort to depress the value of the oil for delivery. The attempt failed, all that the operators were able to accomplish being to lower the quotations for delivery for a few days to the extent of about 1 \( \times \), after which the market immediately recovered and the previous top-figure of 16 \( \times \) was surpassed.

While experienced judges of the market formed the impression that the early, heavy and continuous rains of September would have an unfavourable influence upon the oil-content of the lemons — which of course would have made the position of the article still more precarious, — the mass of operators continued to job gaily on, until an event occurred which no one had foreseen, but of which the effect was to shake the market to its very foundations.

One of the principal and oldest export-firms in Sicily, the very firm which had taken the lead in the bear-speculation mentioned above, and which had sold enormous quantities both locally and abroad, found itself unable to carry out its commitments and, as already hinted, suspended payments, declaring itself unable to supply the goods it had sold. As these sales had been the fulcrum of the whole local speculative movements, the entire structure thereof collapsed, and a panic ensued which was increased by the news that in working up the first parcels of lemons of the new crop, it had become evident that the oil-content of the new fruit was much smaller than that of the two previous seasons.

To add to the complications of the Messina market it became apparent that numerous buyers abroad had placed faith in the reports of certain local firms in
which the prospect of lower prices was steadily being held out, and had consequently refrained from buying. These consumers were now compelled to see to the covering of their own most urgent requirements. No old oil was left, and therefore a wild competition set in for the new oil. Speculators and exporters fought for supplies, and by Christmas they had driven the price of new oil up to 21 a., the manufacturers meantime advisedly keeping back their output, with the object of securing a steady increment in the value of oil. As a result of all these cross-currents of interests, of the appearance on the scene of new speculators who were trying to reap some advantage for themselves out of the market position, and finally, of the continual influx of important orders from the consuming countries, lemon oil wildly advanced in price from Christmas until the end of January, when it reached 30 a., which represents a price even higher than that which was paid for lemon oil somewhere about the year 1859, when the lemon-gardens of Sicily were almost entirely destroyed by a previously unknown disease of the trees.

Since January the prices have receded somewhat. There have been several up-and-down movements and the quotation has now, so to speak, settled down at 28 a. But this does not exclude the possibility that within the next 9 months the figure of 30 a. may again be paid or perhaps surpassed.

Apart from all the misfortunes already recorded, the frosts which in the month of January devastated the lemon- and orange-gardens of California, as well as (it is said) of Spain, have also been fateful for the lemon oil production of Sicily.

Sicilian boxed lemons have not only been in steady and good demand for the North of Europe; they have also realised excellent prices in North America, and there is reason to expect that throughout the present year they will find a steady market there. Hence, large quantities of lemons which would otherwise have been used in the manufacture of oil are not now available for this purpose, being sent out as second-class fruit to the principal consuming ports of Europe and America.

The estimate is not exaggerated, and very possibly it may be below the mark, that as compared with the two previous seasons the output of lemon oil this year will show a decline in quantity of from 30 to 35 p. c. The possibility that this estimate may prove to be below the reality is founded upon the circumstance that, according to all appearances, the small quantity of fruit which still remains on the trees has suffered a not inconsiderable damage from frost during the cold spell which set in after the middle of March, and that therefore the manufacturing operations will come to a premature close.

If we take into consideration the fact that during the last three years, when the crops were in excess of this season's, the consumers abroad have taken up not only the current output but also the old stocks, estimated at 100,000 kilos, there is ground for assuming that notwithstanding the reduced consumption due to the high price of the oil, the entire yield of the present season's crop will certainly be used up to the last drop in the course of the present year, and that therefore a serious decline in prices is scarcely within the bounds of possibility. But if next November or December consumers should happen to find themselves once more wholly dependent upon the product of the coming season's crop, then, no matter how good that crop may turn out, very high prices must be reckoned on in the year 1914.

In order to make it possible to form an opinion of the future course of the trade, it is absolutely necessary to mention another point of importance. The enormous advance in the price of lemon oil during the last 4 months has caused great difficulties and losses to most of the local export houses. Within the last 15 years it had more
and more become customary for foreign buyers to purchase a great part of their requirements for forward delivery before the beginning of the manufacturing season. The exporters in Sicily in their turn were in the habit of covering themselves against such sales by making contracts with the manufacturers.

The heavy losses suffered this year by those export houses which have carried out their obligations in the matter of delivery (several firms are said to have not carried out their engagements or to have done so only partially) have been due to the action of certain manufacturers. Seduced by the knowledge that they could sell their new oil for double the price at which they had undertaken to supply it to the exporters, numerous manufacturers have altogether or in part failed to keep their engagements with the exporters, and the latter, in order to deliver what they had sold, have been forced to purchase the missing quantities elsewhere at high prices on which they lost money. These circumstances, which had never occurred before, have caused the financial position of the manufacturers to be subjected to a more stringent investigation than in the past, and it has been discovered that most of them were unable to give satisfactory security for such large amounts as were represented by this year's transactions. The Sicilian exporters, therefore, will next season be face to face with the problem whether it is or is not possible to continue the present system of selling for delivery. At present it seems that the probabilities are that it will be found impossible to do so.

As regards the prospect of the next lemon crop, all that can be said at present is that the trees are in full leaf and that the copious rainfall of last winter has given them a strong and healthy appearance. The only critical point is that the flowers have developed too far in advance of the season and that later on, in the month of May, the young fruit will be too much exposed to the destructive action of the moist south winds. It is not known at present whether the cold spell and the few nights of frost that have been experienced in some districts have done any serious damage to the trees.

Mandarin Oil. Last season's crop has been a very bad one. High prices have been paid for the fruit for export, and as a result the oil became extremely dear right at the beginning of the time of production.

Orange Oil, bitter. Although the stocks in September of last year were very low, the price of the oil nevertheless declined during the months of September and October from 19 \(\text{\epsilon} \) to 17.75 \(\text{\epsilon} \). In view of the high prices of the fruit these figures left no profit to the manufacturers, and for that reason very little oil has been produced.

The cold, snowy and frosty weather which prevailed here from the beginning until the middle of February has wrought much havoc among the bitter orange plantations, and as a consequence the value of the oil rose rapidly almost from day to day. It will probably advance still further in the course of the summer.

Orange Oil, sweet. In my last report I pointed out that the prospects of the new orange crop did not warrant high expectations. The flowers did not set well, and only a quantitatively small crop was to be looked for. Until well into the month of August the development of the fruit took place under normal climatic conditions, but at an unpropitious moment, in the month of September, extremely heavy rains, unusually plentiful for this part of the world, set in and continued for several weeks. These rains caused the oranges to swell suddenly, a condition which usually has an injurious effect upon the oil-content of the fruit. As a matter of fact, the earliest manufacturing
operations immediately showed the oil-content to be very poor, and both on this account and because the crop was small in respect of quantity, the output has been very restricted and the manufacturers have found it unprofitable to work up the fruit for oil. It is true that the price of sweet orange oil (which, owing to the lack of supplies on the spot, had been maintained at about 18.50 £ during the summer months and even up to the commencement of the new manufacturing season) fell at the commencement of the crop to 16.50 £ and that during this period a few contracts for delivery were concluded at that figure, but a reaction soon set in again and caused the quotations to advance in a few leaps and bounds to 18.50 £, while as early as the middle of December the value of the oil had risen to 20.50 £.

The poor manufacturing results compelled the makers to cease their work earlier in the season than usual, and as almost at the same time a number of enquiries for sweet orange oil were received in our market, an upward tendency was thoroughly justified. Under the influence of this tendency the value of sweet orange oil advanced in the course of December and January and during the first ten days of February up to 25 £. The market then took a duller tone for a few days, after which the quotation again advanced to 25 £.

The stocks which are still held in this country at the present time are unusually small and a decline in the value of this oil is therefore hardly to be expected, rather is it fairly certain that until the arrival of the new crop the market will be dominated by a firmer tendency.

So far as concerns the next crop, the orange trees, like the other essence-yielding trees, are far advanced as compared with other seasons. The foliage is thick and healthy and the flowering promises to be particularly profuse. But even the certainty that the next crop will be plentiful would probably not affect the course of prices of the old oil, as the existing supplies are much too small. If, however, the new fruit matures well and without untoward incidents the prices of the new season's oil for future delivery will certainly be considerably affected and it may be assumed that in that case the new oil will be obtainable at cheap rates.

**Bergamot Oil.** On the constitution of bergaptene see page 149.

**Lemon Oil.** It was to be expected that owing to the present high prices of lemon oil a good deal of adulterated oil would be placed upon the market, but from the numerous samples of sophisticated lemon oil which have been tested in our laboratory during the last few months, we are driven to the conclusion that the practice of adulteration has assumed previously unheard-of dimensions. In most instances turpentine oil was the adulterant, but spirit, mineral oil, lemon oil terpenes, and carvone or orange oil terpenes were also encountered. It is possible that in the case of a few of these samples the oil consisted of a more or less successful synthetic product, for many firms of repute may be tempted to pass off a cheap substitute as a natural oil, or at any rate to use it as an adulterant. We have heard that a Paris firm already well-known in this connection is making direct offers of such a preparation in Sicily for fraudulent purposes. In many instances, however, the "art" of concoction has reached such a height that its products are quite unrecognisable as lemon oil.

We have brought together the characters of the samples in question in the table printed below, mentioning the adulterant in the case of each particular oil. For the rest we may leave the analytical values to speak for themselves, only referring briefly
to sample No. 15. Here we were able to detect the presence of a little spirit, together with a few per cent. of glyceryl acetate, a condition which would scarcely be looked for in the case of an oil of lemon, because there the addition of an artificial ester must in any case be considered as serving no object. Nevertheless it is possible that here the effect of the adulteration was cunningly calculated, for, strangely enough, the constants of the original sample were normal, and it was only after the oil had been shaken out with water that any abnormality was observable, for then it was found that the rotation of the initial 10 p.c. was somewhat in excess of that of the original oil, whereas normally it is less by several degrees; moreover, the sp. gr. had fallen and the rotation had increased. This peculiar behaviour led us to investigate the oil more closely, when, as already stated, it was found to contain spirit and glyceryl acetate, both of which were recovered as such.

Limits of value of good commercial oils.

<table>
<thead>
<tr>
<th>No.</th>
<th>d_{150}</th>
<th>( \alpha_{D20} )</th>
<th>( \alpha_0 ) of the initial 10 p.c. of oil</th>
<th>Citral (est. w. phenyl-hydr.)</th>
<th>Evaporation-residue</th>
<th>Sap v. of evap. res.</th>
<th>Adulterant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0,8604</td>
<td>+ 49° 25’</td>
<td>+ 40°</td>
<td>3,2 %</td>
<td>2,4 %</td>
<td>—</td>
<td>Turpentine oil.</td>
</tr>
<tr>
<td>2</td>
<td>0,8622</td>
<td>+ 40° 15’</td>
<td>+ 27° 50’</td>
<td>3,0 %</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0,8612</td>
<td>+ 50° 9’</td>
<td>+ 42° 20’</td>
<td>3,8 %</td>
<td>2,4 %</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0,8612</td>
<td>+ 52° 15’</td>
<td>+ 40° 10’</td>
<td>2,8 %</td>
<td>1,8 %</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0,8614</td>
<td>+ 51° 11’</td>
<td>+ 46° 17’</td>
<td>2,7 %</td>
<td>2,0 %</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0,8581</td>
<td>+ 51° 5’</td>
<td>+ 52° 18’</td>
<td>—</td>
<td>13,8 %</td>
<td>25,1</td>
<td>Mineral oil.</td>
</tr>
<tr>
<td>7</td>
<td>0,8617</td>
<td>+ 44° 11’</td>
<td>+ 41°</td>
<td>—</td>
<td>12,0 %</td>
<td>44,8</td>
<td>Mineral oil and tur-</td>
</tr>
<tr>
<td>8</td>
<td>0,8676</td>
<td>+ 7°</td>
<td>— 2° 48’</td>
<td>1,5 %</td>
<td>50,4 %</td>
<td>28,5</td>
<td>pentine oil.</td>
</tr>
<tr>
<td>9</td>
<td>0,8690</td>
<td>+ 5° 40’</td>
<td>+ 0° 8’</td>
<td>—</td>
<td>ca. 50 %</td>
<td>10,8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0,8524</td>
<td>+ 57°</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Spirit (about 6 p.c.).</td>
</tr>
<tr>
<td>10a)</td>
<td>0,8565</td>
<td>+ 61° 40’</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0,8525</td>
<td>+ 56° 11’</td>
<td>—</td>
<td>—</td>
<td>2,3 %</td>
<td>—</td>
<td>Spirit (about 6 p.c.).</td>
</tr>
<tr>
<td>11a)</td>
<td>0,8562</td>
<td>+ 60° 10’</td>
<td>+ 57° 46’</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0,8542</td>
<td>+ 63° 34’</td>
<td>+ 58° 42’</td>
<td>2,0 %</td>
<td>3,2 %</td>
<td>—</td>
<td>probably lemon oil</td>
</tr>
<tr>
<td>13</td>
<td>0,8543</td>
<td>+ 83° 44’</td>
<td>+ 76° 52’</td>
<td>—</td>
<td>5,6 %</td>
<td>—</td>
<td>terpenes.</td>
</tr>
<tr>
<td>14</td>
<td>0,8553</td>
<td>+ 94° 26’</td>
<td>+ 93° 22’</td>
<td>1,3 %</td>
<td>2,2 %</td>
<td>—</td>
<td>Carvene or orange</td>
</tr>
<tr>
<td>15</td>
<td>0,8599</td>
<td>+ 59°</td>
<td>+ 55° 44’</td>
<td>—</td>
<td>2,2 %</td>
<td>—</td>
<td>oil terpenes.</td>
</tr>
<tr>
<td>15a)</td>
<td>0,8590</td>
<td>+ 59° 54’</td>
<td>+ 60° 10’</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Spirit and glyceryl</td>
</tr>
</tbody>
</table>

On a disease of Citrus-plants see p. 133.

**Estragon Oil.** We once more beg to recommend the exquisite distillate prepared from herb grown here in Miltitz. We are of opinion that this oil, which is so extremely useful for almost all alimentary purposes, is far from being as much esteemed as it deserves.

1) After shaking out with water.
Eucalyptus Oil. The market-position of Globulus oil, an article which is used everywhere in large quantities, has been steadily firm, and as parcels of importance were only rarely offered from Australia at acceptable prices, buyers were compelled to content themselves with the stocks held in Europe. These were very considerable, although they are now beginning to dwindle, and it appears to be quite possible that sooner or later a serious scarcity may make itself felt. As we have already mentioned on a previous occasion, considerable quantities of eucalyptus oil are now used in Australia in the treatment of mineral ores, and this may perhaps be the principal reason why the producers show so much reserve in offering oil for export. A serious advance in the prices of eucalyptus oil is in our opinion only a question of time, and we strongly advise our friends to cover their requirements before we, too, are compelled to raise our quotations.

Common Australian eucalyptus oil has not been so much in request, but this description is also firm and the imports of it are not in proportion to the sales.

The excellent oil of *Eucalyptus maculata* var. *citriodora* still continues to be favoured by many buyers, although its cost is an obstacle to its use on a large scale. We take this opportunity of once more calling attention to this speciality.

C. T. Bennett\(^1\) again attacks the method of estimating cineol by means of resorcinol, which has been recommended by us\(^2\). He has carried out comparative tests, both by the phosphoric acid and by the resorcinol methods, and has found that the results obtained showed considerable differences, from which he draws the daring conclusion that the resorcinol method, even in its modified form, is not accurate. At the same time he fails to prove the absolute reliability of the phosphoric acid process. Some considerable time ago, as the outcome of similar investigations, Sage\(^3\) formed the same judgment as Bennett has now formed. But even at the time (Report October 1910, 67) we pointed out that in our opinion the difference in the results was precisely a proof of the inaccuracy of the phosphoric acid method, as we had shown, by numerous examples of mixtures with a known cineol-content, that accurate values are obtained with resorcinol provided the test be carried out in the manner described in our Report of April 1908, p. 50. We have seen no reason, since then, to modify our opinion.

In the meantime, F. D. Dodge\(^4\) has published another method for the determination of cineol. This is based upon the familiar fact that, in the cold, cineol remains practically unattacked by potassium permanganate, whereas the remaining constituents of the oils in question (eucalyptus oil and cajuput oil) are oxidised into soluble compounds. The process is carried out as follows: 10 cc. of the oil under examination are placed in a narrow-necked flask, cooled with ice-water, and shaken with a gradually added 5 to 6 p.c. solution of potassium permanganate, until the latter is present in excess. The mixture is then left standing in ice-water for from 12 to 18 hours with occasional shaking, after which the manganese peroxide which has separated out is brought to solution by means of a careful addition of sulphurous acid (or sodium bisulphite + hydrochloric acid). The unattacked oil (eucalyptol) is brought into the neck of the flask, pipetted into a graduated tube, washed with a little alkali, and estimated volumetrically. Its sp. gr. should be 0,929 to 0,930 (15°); it should be inactive, and dissolve in 3,5 vols. 60 p.c. alcohol at 25°.

\(^{1}\) Perfum. and Essent. Oil Record 3 (1912), 269. \(^{2}\) Report October 1907, 45; April 1908, 50. \(^{3}\) Ibidem 1 (1910), 194. \(^{4}\) Journ. Ind. Eng. Chem. 4 (1912), 529; Journ. Soc. chem. ind. 31 (1912), 840; Chem. Zentralbl. 1913, l. 335.
By this method, which he has put in practice for several years, Dodge has obtained satisfactory results with mixtures of eucalyptol, terpenes, and terpineol. In applying it, he has found the eucalyptol-content of eucalyptus oils to be from 52 to 85 p.c. and that of cajuput oils from 50 to 61 p.c. Oils rich in terpenes require about 400 cc. and oils which are poor in terpenes about 100 cc. of the potassium permanganate solution.

C. T. Bennett¹) has experimented with Dodge's method, by making simultaneous control-tests with phosphoric acid and with resorcinol. His conclusion is that although with eucalyptol and eucalyptus oils of high cineol-content approximate results may be obtained, the method is not to be relied upon for cajuput oil and for eucalyptus oils of low cineol-content, as the results obtained were much too high, the reason obviously being that the last-named oils contain constituents which are not entirely oxidised by potassium permanganate in the cold. Bennett carried out his experiments with 5 cc. oil in a cassia flask, whereby he obviated pouring over the non-oxidised portion of the oil.

We have also experimented with the method on artificial mixtures, and have also failed to obtain satisfactory results. It is true that we found that pure eucalyptol almost failed to react with potassium permanganate, but on the other hand it is partly attacked in mixtures containing readily oxidisable substances, as for instance terpineol. Terpineol, we may add, readily reacts with 5 p.c. permanganate solution, giving rise to soluble oxidation-products.

The conditions are different with pinene. Here, if the mixture is at once cooled down at the beginning of the oxidising process, barely-one half of the pinene is oxidised, but if cooling down is delayed until a faint self-heating has set in, and if it is only carried out carefully when the temperature exceeds room-temperature, it is possible to oxidise completely say 5 cc. pure pinene with 200 cc. of the solution. The stability of the terpene towards permanganate is still more markedly shown in the presence of eucalyptol. When the mixture consists of 25 p.c. eucalyptol and 75 p.c. pinene, scarcely any pinene is oxidised during cooling, and even at room-temperature the oxidation is very imperfect and unequal, with the result that far too much eucalyptol is found. Only in the case of a great excess of permanganate, as for instance 1,5 cc. pinene + 0,5 cc. eucalyptol (25 p.c.) to 200 cc. of the solution, all the pinene is oxidised at room-temperature, but at the same time a portion of the eucalyptol is oxidised. In any case it would seem that in oils rich in terpene, the terpenes can only be oxidised with great difficulty, nor does an excess of permanganate mean that the oxidation process is actually terminated. On the other hand, in the case of oils which are poor in terpene, too little eucalyptol is found as a rule, because in such oils part of the eucalyptol is also attacked.

In our estimations we also used cassia-flasks, of course of sufficient size to allow for the addition of enough potassium permanganate, that is to say at least 200 cc. of 5 p.c. permanganate solution for 5 cc. oil.

The results obtained by us are summarised in the following table: —

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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>50 p.c.</td>
<td>1  50 p.c.</td>
<td>1  75 p.c.</td>
<td>682,5 p.c.</td>
<td>67,5 p.c.</td>
<td>27,5 p.c.</td>
<td>607 p.c.</td>
<td>65 p.c.</td>
<td>72,5 p.c.</td>
<td>70 p.c.</td>
<td>62,5 p.c.</td>
</tr>
<tr>
<td>75 p.c.</td>
<td>1  75 p.c.</td>
<td>1  75 p.c.</td>
<td>610,7 p.c.</td>
<td>667,5 p.c.</td>
<td>572,5 p.c.</td>
<td>600 p.c.</td>
<td>60 p.c.</td>
<td>72,5 p.c.</td>
<td>70 p.c.</td>
<td>62,5 p.c.</td>
</tr>
</tbody>
</table>

¹) Perf. and Essent. Oil Record 3 (1912), 295.
Eucalyptus oil employed for medicinal purposes is tested in the various Australian States by different principles. This fact has led W. J. Brownscombe to advocate a uniform method of testing. Brownscombe especially criticises the regulations, based upon the British Pharmacopoeia, under which oils containing phellandrene are excluded from medicinal use. He supports the proposals made by the Federal and Interstate Conference in June 1910, which demand that the only test to be applied shall be that for the presence of aldehydic constituents with b. p. below 120°, of which only "traces" are to be admissible. This demand Brownscombe modifies by fixing a definite maximum content (0.5 p. c.) for such aldehydes, because in his view it is impossible to remove them completely by simple rectification, and because they only impart injurious properties to the oils when they are present in considerable proportions (1 to 2 p. c.). Brownscombe is of opinion that the irritant action of eucalyptus oil is specially due to the presence of these lower fatty aldehydes, but not to that of phellandrene, which, on the contrary, he regards as a therapeutically valuable constituent, because, like piperitone, it imparts antiseptic properties to the oil.

Several years ago), when referring to similar pronouncements by Brownscombe, we pointed out that up to the present it is quite unknown whether the therapeutic value of eucalyptus oil lies in its antiseptic action, and we again wish to lay stress upon this fact.


Oil of Fagara xanthoxyloides. On the constitution of xanthotoxin see p. 149.

Fennel Oil. During the winter-months we have been busily occupied with the distillation of fennel, and even at the present time parcels of importance continue to be received from Galicia at intervals, showing that the disquieting rumours of last September, reporting serious injury to the crop, were not to be taken too seriously. The prices of good quality for distilling have been kept at a very high level, probably rather on account of clever manipulation of the article by speculators, who took good care only to supply the market with just enough fennel to meet the demand of the moment. We know by experience that the reports from this producing district are extremely unreliable, and it is therefore difficult to form a correct opinion of the market, but we are inclined to think that for the present there is no prospect of any lowering of the price of fennel oil, as stocks are not accumulating and the turnover has been very brisk in all varieties. Our two distillates, the qualities of which, owing to our excellent facilities of manufacture, are unsurpassable, are preferred by all consumers who attach importance in the first place to purity of taste. It is very inadvisable to be too keen on "advantageous" purchases in this article, seeing that there are fennel oils in the market of which the employment would simply render the

liqueurs, confectionery, etc. in which they were used unsaleable, and of which the only good point is their “cheapness”.

Galbanum Oil. As a result of the exceptionally high prices which continue to be asked, and which must be paid for galbanum resin, we have been compelled to advance our quotation, and this of course has greatly restricted the sale. It is quite impossible to find enough raw material for the distillation of any important quantities of oil.

Geranium Oils. The scarcity of African geranium oil has not been relieved by the new crop which has come in since our last Report. Most of the Algerian manufacturers have sold their scanty output on contract for several years in advance, and certain wealthy middlemen are taking good care that there shall be no reduction in the price. It is a fact, however, that the consumption has very seriously decreased, since buyers show a quite justifiable reluctance in paying the present fancy-prices. The last quotation was 90 Fr. per kilo, equal to more than 72 £! Most of our customers who formerly bought African geranium oil regularly have taken refuge in substitutes, and they find these answer their requirements so well that it will be difficult to bring them back to the natural oil if ever the price of the latter should again fall to a reasonable level. The export statistics show that the production is steadily declining, the figures having been as follows: —

<table>
<thead>
<tr>
<th>Year</th>
<th>Kilos</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>24,900</td>
</tr>
<tr>
<td>1911</td>
<td>28,500</td>
</tr>
<tr>
<td>1910</td>
<td>33,800</td>
</tr>
<tr>
<td>1909</td>
<td>41,000</td>
</tr>
<tr>
<td>1908</td>
<td>46,000</td>
</tr>
</tbody>
</table>

It is fairly certain, however, that a considerable portion of the output of the years 1909 to 1911 still remains in the hands of certain speculators, who are making it their business to exploit the consumers as much as possible.

In spite of the high range of prices which ruled throughout last year for Réunion geranium oil, business in this article has suffered no reduction worth mentioning, and this is principally due to the scarcity of African oil. The exports from Réunion were as follows: —

<table>
<thead>
<tr>
<th>Year</th>
<th>Kilos</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>43,138</td>
</tr>
<tr>
<td>1911</td>
<td>45,238</td>
</tr>
<tr>
<td>1910</td>
<td>64,156</td>
</tr>
</tbody>
</table>

The starting quotation for oil of the new crop was about 40 Fr., but before long it rose, because the buyers showed themselves far too eager to secure supplies at this surprisingly low figure (last autumn as much as 70 Fr. was paid). The usual sensational reports did their share to advance the market still further, with the result that for the present the value of the oil keeps at about 85 Fr. Unfortunately it is quite impossible to form even an approximately correct opinion of the future of the article; but, basing ourselves upon our experience of the last few years, we incline to the view that there is no chance of a return to the old cheap rates, especially in view of the fact that we have to reckon with the presence of a number of wealthy speculators who, having apparently bought on favourable terms, will do their utmost to maintain values which are so lucrative for them. At the beginning of March we reduced our quotations on the strength of the arrival of new and cheap supplies
which had been secured by us, but in view of the change in the position of the market to which we have referred above, we have been compelled to cancel this reduction.

Our exquisite geranium oil substitute has assisted large numbers of our customers in tiding over the inordinately high oil-prices which prevailed during the winter, and we believe we are justified in predicting a bright future for this preparation.

Thanks to the manner in which the sale of synthetic esters is pushed by certain chemical works, the use of such esters as adulterants of essential oils appears to be constantly on the increase, especially in the case of oils in the evaluation of which the ester-value plays no decisive part. In our last Report, p. 92, we called attention to an adulteration of petitgrain oil with terpinyl acetate, and on the present occasion we have to report on similar sophistications of other oils. In a (probably artificial) oil of lemon (p. 60), we found glycerylacetate; in samples of rose oil (p. 83) and of African geranium oil we detected phthalic ester. The last-named sample, like the others, had been submitted to us for our opinion. Its constants were as follow: 
\[d_{150} 0.9303, \alpha_0 - 5^\circ 22', n_d 1.47397,\text{ acid v. 4.3, ester v. 128.8 = 54.3 p. c. ester, calc. for geranyl tiglate, sap. v. 133.1, acid v. II}^{1)} 34.8, \text{ ester v. after acet. 276.5 = 95.9 p. c. calc. as total geraniol, sol. in 1.6 vols. a. m. of 70 p. c. alcohol. These analytical figures pointed unquestionably to the fact that the oil was adulterated, especially because the ester-value and the percentage of alcoholic constituents were much too high. Further evidence of sophistication lay in the great difference between the sap. v. and the acid v. II of the oil. In the case of a sample of pure African geranium oil which was tested for purposes of comparison this difference was only 0.9; in the oil under examination it was 98.3. From this it was evident that either a fatty oil or the ester of a sparingly volatile acid had been added to the oil, and as the first-named addition was excluded by the ready solubility of the sample, the second remained the only possibility. Further examination revealed the adulterant as a phthalic ester; probably ethyl phthalate, an easily obtainable compound, for when the acid v. of the acid which had not passed over with steam was estimated, it was found to be identical with that of phthalic acid. Recrystallised from water, this acid had m. p. 200 to 203°; it sublimed with elimination of water in the long needles, m. p. 129°, which are characteristic of phthalic anhydride; melted up with resorcinol and zinc chloride it afforded fluorescène. The proportion of added ethyl phthalate was estimated from the difference between sap. v. and acid v. II to be about 20 p. c.

On p. 480 of the issue of August 3rd, 1912 of the Revue agricole & viticole de l'Afrique du Nord, a journal published in Algiers, Jolivet publishes an article on the cultivation of the geranium plant in Algeria. We can only refer to the article here for the purpose of recording its appearance, as we have already dealt at length with the cultivation of geranium in previous Reports.

On the properties of Australian geranium oil, see p. 122.

**Ginger Oil.** At last we are able to record a change for the better in the position of this article, for, owing to satisfactory crops, all descriptions of ginger suitable for distilling have receded in value. It has been possible to reduce the prices by about

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10 p.c., but as there is a very sustained demand for our distillate, no further decline in our quotations is probable. The principal raw material for distilling has been African ginger, which has gradually fallen in price from about 80 $\text{M}$ at the beginning to 48 $\text{M}$ at the end of the year.

Several years ago H. von Soden and W. Rojahn succeeded in isolating from the first runnings of ginger oil an aldehyde which they were unable to identify more closely, the available quantity being too small. It is possible that this body may be identical with an aldehyde which has been obtained by F. D. Dodge, to the extent of from 2 to 5 p.c., from the low-boiling fractions of Jamaica ginger oil by shaking out with neutralised 15 p.c. bisulphite liquor. After shaking out, Dodge allowed the mass to stand for a few days at a low temperature. The aldehyde recovered by steam-distillation from the bisulphite-compound after treatment with the calculated quantity of sodium bicarbonate constituted a colourless, very mobile liquid, possessing a characteristic odour of oranges or of decylaldehyde: $d_{15}^0 0.828$, $\alpha_2$ inactive. It is very sensitive towards alkalis, hence the regeneration from the sulphite-compound is not always successful. The semicarbazone melts at 98° (from methyl alcohol). The oxime was prepared by Mannich's method and had m.p. 63° (from dilute alcohol). The nitrile was prepared from the oxime by boiling with acetic anhydride. Its odour reminds of oil of rue. The acid which was yielded by the nitrile had m. p. 50°, and gave acid value 313.9 (calc. for $C_{10}H_{50}O_2$ 325.3; for $C_{11}H_{22}O_2$ 301). Dodge supposes the aldehyde to be identical with the $n$-decyllic aldehyde of oils of orange, cassie, orris, and coriander.

When the aldehyde is kept for a prolonged period molecular transpositions would appear to take place in it. For example, one portion of it, after having been kept for over nine years in a well-stoppered bottle, failed to react, at the end of that time, either with bisulphite or with semicarbazide. Nor was the conversion-product (which possessed a well-defined geraniol odour), attacked by chromic acid solution.

Gingergrass Oil. Business in this article has continued to drag, but the prices have remained unchanged because the supplies brought to market have not been inordinately heavy. Nowadays this oil by no means plays the important part it used to do.

Guaiac wood Oil. The stocks are again rapidly approaching depletion, and higher prices are being asked for the wood, for which reason we regard an improvement in the value of the oil in the course of a few months as probable. For the moment we need make no change in the quotations of our oil, which is always in fresh condition.

Gurjun balsam Oil. Of the botanical origin of gurjun balsam it is known that the drug is derived from several species of *Dipterocarpus* (in particular from *D. turbinatus*, Gærtn. fil., *D. ineanus*, Roxb. and *D. alatus*, Roxb.; N. O. *Dipterocarpaceae*), but up to the present nothing has become known of the balsams produced by these different species; hence we are in complete ignorance whether, and if so in what respect, they differ from each other. On this account it afforded us great satisfaction to be given an opportunity recently of making the acquaintance of gurjun balsams derived from authentically determined species of *Dipterocarpus*. The occasion was the publication of an official report by R. S. Pearson on Indian Forest products, in which in the

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chapter "Oil-Resins", he refers to two gurjun balsams, one of which is derived from Dipterocarpus turbinatus and the second from *D. tuberculatus*.

Through the courtesy of Mr. C. G. Rogers, Conservator of Forests at Rangoon, Burma, we were able to procure samples of these two balsams, of which the following particulars may be given: —

*Dipterocarpus turbinatus*, Gærtn. fil. is a large tree which is found throughout tropical Burma, in Bengal, and on the Andaman Islands. Its balsam is specially known there by the name of "gurjan oil". It is collected in large quantities and is used as a paint for houses and ships, as well as a preservative for articles of bamboo. The balsam is exported from Chittagong (Bengal). The sample received by us consists of a faintly acid, milky liquid; acid v. 10,9; sp. gr. 0,9811 (15°). When allowed to stand, especially in the warmth, it separates out into a brown oil which floats on the surface and a viscous, whitish-grey, emulsion-like mass. The constants of the oily layer were as follow: $d_{150} 0,9706$, $\alpha_d -10^\circ 8'$, $n_{D20} 1,51200$, acid v. 7,3, ester v. 1,9. By steam distillation we succeeded in separating out from the total balsam 46 p.c. of a pale-yellow oil of a balsamic odour, possessing the following constants: $d_{150} 0,9271$, $\alpha_d -37^\circ$, $n_{D20} 1,50070$, acid v. 0, ester v. 1,9, sol. in 7 vols. a.m. 95 p.c. alcohol.

*Dipterocarpus tuberculatus*, Roxb. yields a balsam of very different appearance. It is known in Burma as "in oil", and plays a very subordinate part compared with "gurjan oil". The balsam is of a pale-brown colour; its consistency is that of turpentine and its sp. gr. at 15° is 1,029; acid v. 17,8; ester v. 0. The oil which was separated out from it by steam-distillation (yield 33 p.c) was of a yellow-brown colour, and dissolved in 6 vols. a.m. of 95 p.c. alcohol. Its constants were as follow: $d_{150} 0,9001$, $\alpha_d -99^\circ 40'$, $n_{D20} 1,50070$. It did not contain saponifiable constituents (sap. v. 0). With Turner's colour-reaction both the balsams and the oils gave the characteristic violet colour. This test consists 1) in dissolving 3 or 4 drops of the balsam or oil in 3 cc. of glacial acetic acid, adding to the solution 1 drop of freshly-prepared 10 p.c. sodium nitrite solution, and layering the mixture very carefully on 2 cc. of concentrated sulphuric acid. The test has been somewhat modified by Deussen and Eger.

Another balsam, which is greatly esteemed in Burma, and of which we have also received a sample, was derived from *Melanorrhoea usitata*, Wall. (N. O. Anacardiaceae). It consisted of a thick, viscous, brown mass with an odour of train-oil. It turned black when exposed to air. This balsam, which is known as "thitsi oil" is of no interest for us, as it contains no essential oil whatever.

**Juniper berry Oil.** A few claims due to the imperfect solubility in weak alcohol, of extra-strong juniper berry oil, give us occasion to point out once more that the solubility of juniper berry oil 2) soon begins to diminish during storage, and that extra-strong juniper berry oil possesses the same peculiarity. It is not impossible, however, that oils of the 1912 crop may possess the property of resinification in an exceptionally high degree, because in that year the yield of oil and of juice, as compared with the yield from raw material of other seasons, was quite abnormal, and the sugar-content of the juice was low, no doubt as a result of the cold and rainy summer.

We are now engaged in making experiments with the keeping-properties and solubility of extra-strong juniper berry oil, and we intend to return to the subject in due course, and to give practical hints for the storage of juniper berry oil.

Oil from the Berries of Juniperus phœnicca. An English periodical\(^1\) gives constants of an oil distilled in Cyprus from the berries of Juniperus phœnicca, as follow: \(d\ 0,867, \alpha_d + 5°, n_d=1,4708\). We ourselves many years ago described an oil of which we obtained a yield of 1 p.c. from a variety of red juniper berries imported by us from Smyrna. The characters of this sample were as follow: \(d_{160} 0,859; \alpha_d - 4° 55'\).\(^2\)

Lavender Oil. Since the last crop the lavender oil market has only shown slight fluctuations and during the winter the turnover has moved within moderate limits. A number of producers have thought it advisable to withhold their lavender oil from the market because, as a result of the familiar absurd stirring-up of popular feeling against our firm, they had come to believe that an upward movement was impending. In these expectations they have been severely disappointed. Apart from this, a fair quantity of oil is available, and at times it is possible to buy below the market-price when a speculator here or there is under the necessity of realising. If the stagnation on the lavender oil trade should continue, it is to be expected that this year a heavy stock of oil will have to be carried forward into the new season, and this circumstance would of course weigh in determining the value of the present year's oil. It is a well-known fact that for many seasons past the new oil has always been looked forward to with great eagerness, as the previous year's output was invariably used up to the last drop.

It is to be regretted that the practice of adulterating lavender oil has lately assumed what must be described as fearful dimensions. Our laboratory-books record a rich selection of examples of more or less skilful adulteration. We strongly urge our friends, in so far as they have covered their requirements by purchases made in the South of France, to send samples of such parcels to us for examination. The services of our laboratory are gratuitously at the disposal of our clients, and everyone who avails himself of them renders an invaluable service, not only to himself, but first of all to the trade at large. It is extremely difficult for a perfumer to detect adulterations consisting of the addition of foreign esters, and it is precisely sophistictions of this kind that have recently been the order of the day.

An article by one Marcel Provence, entitled "Les Allemands en Provence", appeared last October in Les Quatre-Dauphins, a monthly review, and was reprinted in several local papers in the South of France. Its object apparently was to stir up animosity against our works at Barrême among the population of the lavender districts. We would take no notice here of this attack, which is thoroughly characteristic of the tactics of the French chauvinist press, were it not that we cannot bring ourselves to deprive our readers altogether of this comic contribution — for as such every normally constituted person, no matter what may be his nationality, will regard it. The author depicts what he saw on the occasion of a visit which (without permission, by the way) he paid to our factory at Barrême. He grows excited because the greater part of the installation came from Germany. But the special object which provoked his indignation was a harmless ornament in the gable of the building, which owes its existence to the fancy of our French architect, but in which this patriotic writer espies the likeness of a German soldier's peaked helmet! But even this is not enough. The fact that our peaceful little factory is only 25 metres distant from the railway should, he thinks, afford grave cause of misgiving, for "strategic reasons". It is therefore obvious that

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\(^1\) Perfum. and Essent. Oil Record 3 (1912), 291. — \(^2\) Report October 1895, 30.
we are believed to contemplate a military attack upon the little "back-block" line from Puget to Théniers and Digne! The article in question brims over with these and similar horrors! We have been much amused by it, especially because we have heard that it was inspired by one of our competitors in the South of France. But how poor an opinion must an author have of the intelligence of his readers that he should dare to dish up such rubbish to them! Fortunately we have a better opinion of the people of Barrême, to whom the establishment of our works has brought nothing but advantage, and we know how they look upon such libels. M. Marcel Provence might have spared himself this public exposure!

We have recently isolated from French lavender oil of our own distilling a fraction possessing the following constants: b. p. 89 to 90° (3 mm.), d₁₅₀ 0,9008, αᵥ + 0°.49', n₂₀₀ 1,49856. As these constants pointed to caryophyllene we hydrated the oil by heating it with glacial acetic acid and sulphuric acid, and obtained caryophyllene alcohol, m. p. 93 to 94,5°. The phenylurethane had m. p. 136 to 137° (from methyl alcohol). This investigation demonstrates the presence of caryophyllene in lavender oil.

Lemongrass Oil. It would seem that the result of the crop has been very satisfactory, for there has certainly been no lack of offers. On the other hand these offers encountered an animated demand, which prevented a slump in prices. According to the supplies available and the demand of the moment the quotations fluctuated between 3 d. and 4 d. per oz. and business is described as being very brisk. As is shown by the statistical table at the foot of the paragraph, the shipments via Cochin in 1912 exceeded those of 1911 by about 100000 lbs. The bulk was again shipped to Marseilles, whence it is probably forwarded to Switzerland. A few small parcels have also been received from Java, but as the solubility of this oil proved to be imperfect, it only found buyers at a corresponding reduction in price.

The shipments from Cochin have been distributed as follows:—

<table>
<thead>
<tr>
<th>Port of Destination</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1911</td>
</tr>
<tr>
<td>London</td>
<td>11 550 lbs.</td>
</tr>
<tr>
<td>Liverpool</td>
<td>—</td>
</tr>
<tr>
<td>Havre</td>
<td>28 644</td>
</tr>
<tr>
<td>Marseilles</td>
<td>70 191</td>
</tr>
<tr>
<td>Bremen</td>
<td>3 019,5</td>
</tr>
<tr>
<td>Hamburg</td>
<td>17 473,5</td>
</tr>
<tr>
<td>New York</td>
<td>13 645,5</td>
</tr>
<tr>
<td>Total:</td>
<td>144 523,5 lbs.</td>
</tr>
</tbody>
</table>

Parry¹) has examined numerous West Indian and Cochin lemongrass oils and has found that in the course of time the citral value of these oils declines somewhat. West Indian oils which had originally contained from 78 to 80 p. c. of citral, after some years' keeping showed a drop of from 4 to 5 p. c. With East Indian oils the reduction in the citral value takes place still more rapidly; shipments which contained from 75 to 78 p. c. of citral when they left Cochin only contained from 69 to 73 p. c. upon their arrival in Paris and London two months afterwards. Parry is of opinion that the constancy in direction of the reduction excludes the possibility of error in testing in the

¹) Perfum. and Essent. Oil Record 4 (1913), 40.
East, and the number of samples examined was much too large to admit of such an explanation. Moreover, not only the East Indian but also the West Indian oils showed a diminution in solubility. He leaves it an open question whether this is an accident or whether it is connected with the drop in the citral value.

What surprises us in Parry's discovery is that in no case has he found the difference to exceed 5 p.c. From this it would appear that the drop in citral value is very soon arrested, possibly because the products which are formed in the process of alteration of the constituents of the oil have a preserving effect upon the citral. We may add that a sample of lemongrass oil from Barbados, which is described in our Report of November 1908 (p. 82) was found by us after a lapse of 2 years to have the same aldehyde-content as when we first examined it (85,5 p.c. with neutral sulphite or 90,5 p.c. with bisulphite). In this case also there was no change in the conditions of solubility, which appears to support the supposition that diminution of solubility goes hand in hand reduction of citral value.

In our Report of April 1912, p. 89, we mentioned several samples belonging to the group of sparingly-soluble lemongrass oils, which had been examined by the Imperial Institute of London. Among other places, these oils came from Ceylon and British India (Wahjain, Prov. of Assam). Since then the Imperial Institute has received from the same districts fresh samples of lemongrass oils of which the constants were similar to those previously examined. With 70 p.c. alcohol the samples gave no clear solution. For the rest their behaviour was as follows:—

<table>
<thead>
<tr>
<th>Origin</th>
<th>$d_{150}$</th>
<th>$\alpha_{D}$</th>
<th>Citral content (Bisulphite method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceylon</td>
<td>0,9109</td>
<td></td>
<td>73,7 p.c.</td>
</tr>
<tr>
<td>India, Tyrna</td>
<td>0,9039</td>
<td>$0^\circ 30'$</td>
<td>72,2 &quot;</td>
</tr>
<tr>
<td>India, Cochin</td>
<td>0,9035</td>
<td>$0^\circ 40'$</td>
<td>81,5 &quot;</td>
</tr>
<tr>
<td>India, Mariani</td>
<td>0,8973</td>
<td>$0^\circ 20'$</td>
<td>78,0 &quot;</td>
</tr>
</tbody>
</table>

Another example of the sparingly-soluble lemongrass oils is represented by a distillate from Burma described in the Perfumery and Essential Oil Record. This sample was soluble in 90 p.c. alcohol with slight opalescence; sp. gr. 0,893 (15°C); citral-content 74 p.c. The author of the article in the journal in question expresses the surmise that the imperfect solubility of the oil is due rather to the conditions of the weather prevailing during the cutting of the grass than to differences in the actual species of the grass from which the oil was distilled. He bases this view upon the fact that the yield of oil from the grass is less during the dry than during the rainy season, and he expresses the hope of being able to give further particulars on this subject, because he has been promised samples of oil distilled under both conditions.

Together with the oil above-mentioned, the author describes two other samples, also Burmese; the product of “sweet-scented lemongrass”. This oil, in its general characters, is more akin to Java citronella oil. Of the two samples one had sp. gr. 0,893, total geraniol-content 91,5 p.c. while in the other ($d_{150}$ 0,896) the total content of acetylisable constituents was estimated at 101,5 p.c. It was also found that the proportion of citronellal in the second sample very considerably exceeded that of the geraniol.

In Burma the oil is used as a household remedy for the cure of almost every complaint. It is asserted to possess antiseptic properties.

In connection with the above we may here refer briefly to a few samples of lemongrass oil which have been received by us from Formosa and Celebes, which were also noteworthy for their poor degree of solubility:—

**FORMOSA OILS.**

<table>
<thead>
<tr>
<th>( d_{150} )</th>
<th>( a_p )</th>
<th>Aldehyde-content</th>
<th>Bisulphite</th>
<th>Sulphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,9139</td>
<td>±0°</td>
<td>75 p.c.</td>
<td>Sol. in 2,5 vol. 70 p.c. alc. a.m. Dilute sol. opal.</td>
<td></td>
</tr>
<tr>
<td>0,8821</td>
<td>—0°8'</td>
<td>76 p.c. 66 ''</td>
<td>Sol. in absol. alc. to 1 vol., afterw. turb.</td>
<td></td>
</tr>
<tr>
<td>0,8654</td>
<td>—0°4'</td>
<td>54 '' 50 ''</td>
<td>Sol. in 95 p.c. alc. to 0,5 vol., afterw. turb.</td>
<td></td>
</tr>
<tr>
<td>0,8664</td>
<td>—0°4'</td>
<td>56 '' 53 ''</td>
<td>Sol. in 95 p.c. alc. to 0,5 vol., afterw. turb.</td>
<td></td>
</tr>
<tr>
<td>0,8836</td>
<td>—0°6'</td>
<td>69 '' 65 ''</td>
<td>Sol. in absol. alc. to 1 vol., afterw. turb.</td>
<td></td>
</tr>
</tbody>
</table>

**CELEBES OIL.**

0,8799 | —0°15' | 67 p.c. | Even in absol. alc. only clearly sol. at first.

It is remarkable that with one single exception, in which the specific gravity is strikingly high, these oils are all very light, and that almost all of them are poor in citral. This, however, is a peculiarity which is often observed in these distillates, which appear in commerce under the generic name of „West Indian lemongrass oils”

Two lemongrass oils from the island of Mayotta, described by the firm of Roure-Bertrand Fils, may here be mentioned. Their characters were as follow: \( d_{150} \) 0,9072 and 0,8877, \( a_p \) —0°4' and —0°6', aldehyde content (estimated by the bisulphite method) 75,5 and 78 p.c. The oils were not soluble in 90 p.c. alcohol, and even with 96 p.c. alcohol they only gave a clear solution at the beginning. It follows that they belong to the group of sparingly-soluble so-called West Indian lemongrass oils.

**Limette Oil.** We have succeeded in securing a few parcels, but only by paying high prices. These high values are due on the one hand to the advance in Sicilian essences and on the other to the drought from which (so our West-Indian purveyor informs us) the producing districts have suffered severely.

It is generally known that distilled limette oil is quite different from the hand-expressed oil (hand-pressed lime oil), the first-named oil having a disagreeable, turpentine-like odour, which is no longer reminiscent of citral. H. A. Tempany and N. Greenhalgh, who have investigated the matter, are of opinion that the difference is caused by the loss, during the process of distillation, of part of the lowest- and highest-boiling fractions. They distilled hand-expressed oils with steam, and obtained an oil with the characteristic turpentine-like odour of the distilled oil of commerce. The highest-boiling fractions of the hand-expressed oil contain a blue fluorescent, crystalline body (perhaps methyl anthranilate), which is absent from the distilled oil.

1) The first sparingly-soluble lemongrass oils placed upon the market came from the West Indies. —
Moreover, limettin, which ordinarily separates out from the hand-expressed oil when it is left standing, is also absent from the distilled oil. As a rule the citral-content of the distilled oil is lower than that of the hand-expressed oil. The authors have found authentic samples to show the following properties:

I. Hand-expressed oils: \( d_{50} \): 0,8712 to 0,8859, \( a_{D}^\text{H} \): 31,38 to 33,43° (+ ?), \( n_{D}^\text{H} \): 1,4789 to 1,4851, acid v. 1,35 to 2,8, citral content \( n \) 2,2 to 6,6 p.c.

II. Distilled oils: \( d_{50} \): 0,8540 to 0,8858, \( a_{D}^\text{H} \): 33,09 to 34,89°, \( n_{D}^\text{H} \): 1,4702 to 1,4713, acid v. 0,76 to 1,3, citral content \( o \) 1,2 to 2,0 p.c.

Distilled limette oil is obtained as a by-product in the evaporation of lime-juice. In our opinion the citric acid, during this process, acts destructively upon the constituents of the limette oil, and enters into combination with the anthranilate, which would account for the inferior quality of distilled limette oil. Possibly, too, the hand-expressed oil distilled by Tempany and Greenhalgh may not have been entirely free from citric acid.

The superficial area of the island of Dominica is about 304 square miles. Of this area about 17618 acres are under cultivation, of which about 5000 acres hectares are planted with lime trees. Both climate and soil are excellently adapted for the growing of limes\( ^2 \). In the course of the last 30 years the lime-industry has rapidly developed in the island. The first plantations date back to the year 1850.

In the year 1910, 5761 gallons of distilled and 1018 gallons of hand-expressed limette oil (oil of limes) were exported, representing a value of \$ 16823 and \$ 11767 respectively. In the year 1911 the exports reached 5472 gallons of distilled and 892 gallons of hand-expressed oil, to the value of \$ 15989 and \$ 10317 respectively.

According to H. A. Tempany and T. Jackson\( ^2 \) the climate and soil of the island of Antigua are less well suited for the cultivation of limes, although the natural conditions there can by no means be described as bad. Within recent years the shipments of limes from Antigua have greatly increased. The authors say nothing about the preparation of limette oil in this island; it would appear that only the fruit is exported from it.

**Linaloe Oil.** In view of the fact that no stocks were accumulating, and that the Hamburg importers had no difficulty in disposing of their consignments of Mexican oil, a decided improvement in values became perceptible as early as the end of last year, and an advance of several marks per kilo had to be conceded. The scarcity of bergamot oil was followed by such a demand for linalyl acetate- and bergamot oil-substitutes that all the arriving raw material found buyers from various quarters waiting to secure it, and a corresponding reaction took place in the course of prices. The same conditions have resulted in an extremely sustained demand for Cayenne linaloe oil, of which the arrivals found ready buyers at prices which at last must have left a profit to the manufacturers. We hear from Cayenne that there has been strong competition for the wood and that there is no prospect of any lower prices for the oil. A few parcels of Cayenne linaloe wood, which have been held in consignment in Europe for the past two years, made their appearance from time to time without finding a buyer.

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\( ^1 \) Determined by Burgess and Child’s method, (comp. Report April 1902, 33). For the properties of the oil also compare our Report of October 1909, 77. — \( ^2 \) Daily Consular and Trade Reports, Washington. —

\( ^3 \) West Indian Bulletin 12 (1912), 504.
We take the following statistical data referring to Cayenne linaloe oil from an American journal\(^1\). The exports from French Guiana were as follows:

<table>
<thead>
<tr>
<th>Year</th>
<th>Wood</th>
<th>Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>1909</td>
<td>265 tons, value 19,875 Fr.</td>
<td>12,497 kilos, value 312,400 Fr.</td>
</tr>
<tr>
<td>1910</td>
<td>1262 &quot; &quot; 94,628 &quot;</td>
<td>22,066 &quot; &quot; 551,650 &quot;</td>
</tr>
<tr>
<td>1911</td>
<td>209 &quot; &quot; 20,175 &quot;</td>
<td>46,642 &quot; &quot; 1,075,050 &quot;</td>
</tr>
</tbody>
</table>

It would seem that in 1910 1000 tons of wood of another kind were erroneously entered in the Customs' declaration as linaloe wood, which explains the abnormal figures for that year.

The statement on p. 78 of our last Report that linalool oxide occurs in Cayenne linaloe oil is unfounded. We have actually proved the presence of the oxide in Mexican linaloe oil only.

Marjoram Oil, see Origanum Oil, p. 76.

Matricio Oil. This oil has been wanting for a considerable time, but a few weeks ago we succeeded at last in discovering a parcel of leaves suitable for distillation, with which we have been able to replenish our stock of matricio oil. We wish to call special attention to this fact, the more so because the newly-distilled oil is well worth its price. We are in a position to supply quantities of some importance at advantageous prices.

Mentha Oils. Some time ago Prof. Tschirch, of Bern, sent us several species of Mentha which had been collected and botanically identified by him, with the request to determine whether or not any of them contained menthol. We thus had an opportunity of preparing oils from absolutely authentic and uniform samples of Mentha aquatica, L. and M. silvestris, L., a matter which is of special interest because these oils are little, if at all, known. Unfortunately the samples available of the separate herbs were very small and we were therefore only able to prepare a few cc. of each oil, so that the examination and determination of their physical constants was necessarily very restricted. We give below, however, the results obtained:

Oil from Mentha aquatica, L. The dried herb, when distilled, afforded 0,8 p.c. of a pale-yellow oil with a faint odour of mint; \(d_{150} 0,9553; \alpha_D +64^\circ 56'; n_{D20} 1,48276\)\(^9\).

Oil from Mentha silvestris, L. Yield 0,9 p.c. Pale yellow; odour somewhat insipid, faintly mint-like; \(d_{150} 0,9852; \alpha_D —132^\circ 52'; n_{D20} 1,46856\). We were unable to detect menthol in either oil, but as only minute quantities of the oil were available we must leave it an open question whether menthol is really totally absent. So much at any rate is certain that the oils can only contain traces of it at the most. The same applies to an oil prepared from Mentha viridis, L. (yield 0,17 p.c.; \(d_{150} 0,9512; \alpha_D —52^\circ 5')\).

Oil of Mosla japonica. Nurayama and Nara\(^9\) have discovered that the oil of Mosla japonica, Maxim. \((N. O. Labiatae)\) contains \(\alpha\)-pinene in addition to its previously-known constituents, carvacrol, and \(p\)-cymene\(^4\).

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\(^1\) Amer. Perfumer 7 (1912) 250. - \(^2\) An oil of water mint, referred to in Gildemeister and Hoffmanns work The Volatile Oils, 1st ed., p.654, gave quite different constants: \(d_{20} 0,880, \alpha_D — 29^\circ 14'). — \(^3\) Journ. pharm. Soc. of Japan 1912; Chemist and Druggist 82 (1913), 19. — \(^4\) Comp. Report April 1910, 78.
**Mustard Oil.** The position of this article remains unchanged, and within the past six months the fact, already previously pointed out by us, that the use of genuine oil has decreased in favour of that of artificial mustard oil, has been confirmed. Our output of the latter is increasing rapidly, but prices are firm, as the raw material has in part experienced a not inconsiderable advance in price.

On the occurrence of myrosine and allyl isosulphocyanate in cauliflower seeds see p. 108.

**Neroli Oil.** An exceptionally mild winter has greatly assisted in promoting the normal development of the trees, and unless excessive drought or late night-frosts should set in a very good crop, scarcely falling below that of last season, may be expected. The total quantity of flowers produced in 1912 in the South of France is estimated at from 2800000 to 2900000 kilos and of this total, as stated in our last Report, 1900000 kilos fell to the share of the Société Coopérative des propriétaires d'orangers. The excessive production of flowers injuriously affected their sale to distillers, with the result that the Society found itself compelled to work up 800000 kilos for its own account. Great dissatisfaction has naturally been caused among the members of the Society by the fact that the owners of orange-trees who refrained from throwing in their lot with the Society have done better last year than the members themselves, and the general meeting convened for March 30 is to decide whether or not the distillation of neroli oil in the works belonging to the Society is to be given up, and whether it will not be better to sell the flowers to distillers at prices at which it will not pay them to grow them themselves. In that case the price of the flowers would no doubt fall to 40 or 45 centimes per kilo, which would be equivalent to a price of about 300 Fr. per kilo for neroli oil. If the majority should decide to continue the present method of working, it would be necessary to extend the Society's own distilling plant still further, but in that case the Society would at least be able to allow its members from 60 to 70 centimes per kilo of flowers, which would be ample to cover the cost of cultivation. The price of neroli oil of the season 1913 would in that case figure out at from 350 Fr. to 400 Fr. per kilo, which would be about the same as in 1912. It is to be hoped that an agreement will be reached between all the interested parties, for if not, it is quite on the cards that the cultivation of orange-trees in the South of France may be abandoned as no longer a paying business. We are regretfully compelled to withhold the report of the result of the general meeting until our next Report; but this much is already certain that, given normal conditions of weather, genuine neroli oil will again be obtainable this year at advantageous prices.

**Nutmeg Oil.** The difficulty of procuring nutmegs with a satisfactory oil-content at reasonable prices made itself so seriously felt within the last few months that the long-expected increase in prices became an actual fact. In spite of the advance, however, the oil is selling very briskly indeed, for it would appear that the cheap stocks in consumers' hands are quite exhausted. Large orders received from the United States could only be executed with considerable delay, but for some time past distilling has been again in progress at our works at a full pace, and the scarcity of oil is therefore a thing of the past. It is probable that for some time to come prices will remain at their present level, for it still continues difficult to find nutmegs which are suitable for distilling.
Bark Oil from Ocotea (Cryptocaria, or Mespilodaphne) pretiosa. A sample of the bark of Ocotea pretiosa, Benth. (Cryptocaria pretiosa, Mart.; Mespilodaphne pretiosa, Nees et Mart., N. O. Lauraceae), which has been sent to us, was distilled and yielded 0.83 p. c. of a brown oil of cinnamon-like odour. Its sp. gr. was 1.1200 (15°) and its refractive index 1.52712 (20°); owing to the dark colour it was not possible to determine the rotation. It was soluble in 6.5 vols. a. m. 80 p. c. alcohol. It is probable that its constituents do not include esters, but lactone-like compounds, for when 1.5 gram of the oil was saponified, 5 cc. seminormal potash solution was first used up, but after neutralisation a fresh separation of alkali immediately took place and in the end the saponification value 0 was obtained. Acetylation could not be carried out, as with acetic anhydride a violent reaction ensued, gas being given off and carbonification taking place. The presence of lactones and perhaps also of phenols is furthermore indicated by the fact that the oil is partly absorbed by soda liquor, about 65 p. c. of the oil going into solution when shaken with 5 p. c. liquor. When dilute sulphuric acid was added to the deep red-coloured solution an oil separated out which was at first of a yellow colour, but which very quickly turned darker. So far we have obtained no particulars with regard to the character of this oil, except that we found it to be strongly nitrogenous. Judging by its odour, the portion of the oil which did not react with sodium hydroxide contains caryophyllene.

As in the case of an oil previously distilled by us¹ so in the present sample, no cinnamic aldehyde could be detected, in spite of the fact that its presence was suspected from the odour.

The bark came from Brazil, where it is used as a remedy in gout. With regard to the oil distilled from the branches and the wood of Cryptocaria pretiosa, comp. our Report of April 1911, 83.

Origanum Oils. How the naming of oils from the vernacular names of the parent-plants from which they are derived can lead to confusion is shown by E. M. Holmes² in the case of marjoram. In France Origanum vulgare and O. majorana are distinguished by the names of marjolaine sauvage and marjolaine douce. In Southern France Calamintha Nepeta is also frequently called marjolaine instead of Calaminthe nepête, a fact which leads to oil of Calamintha Nepeta being frequently brought into commerce under the name of marjoram oil³. Holmes gives a detailed botanical description of Origanum majorana, L. and Calamintha Nepeta (lesser calamint) together with clear illustrations of the entire plant and the flower-parts.

Origanum majorana (sweet marjoram) was grown as a pot-herb by the ancient Egyptians. It is perhaps a native of the Southern Mediterranean region. The oil is now chiefly manufactured in Spain. Willdenow describes a variety of this species as Origanum majoranoides¹. The last-named species has been photographed by Holmes⁵ from material collected in Cyprus and now in the Kew Herbarium. This species, as well as O. Onites, L., O. maru, L. and O. hirtum, Lk., is said to furnish the origanum oil of commerce. In all probability other species are also distilled, but of these little is as yet known for certain.

We have recently distilled so-called Spanish-hop oil (origanum oil) from authentic raw material, consisting of Majorana Onites, (L.) Benth. (Origanum Onites, L.; O. smyrneeum, L.) and Origanum hirtum, Lk., a albiflorum, Hssk.⁶.

**Orris Oil.** We quote below, as usual, our correspondents' report on the Florentine orris root market:—

"The figures which we mentioned in our last report to your firm have proved to be correct. According to various statistics, and judging from the particulars which we have gathered in the course of our constant intercourse with the producers, and of which we are able to test the accuracy, the total output of root last season has not been more than 600 tons.

Up to the end of February 1913 France (which has been a large buyer), Germany, England and America have taken together 520 tons.

Leaving a balance of 80 tons.

Of this balance nothing now remains in the hands of the producers. The bulk is controlled by speculators, who began by degrees to buy up small lots in the producing centres in the month of October, and by these manipulations succeeded in raising the price of orris root up to 160 Lire (≈130 £) per 100 kilos, delivered at the station at Florence. The speculators in question made their purchases simultaneously in different localities, mostly from small growers, and by this ruse they were able to secure the root at the lowest possible price. When once the parcels were under their control they set about to cause an advance in the foreign markets. Foreign buyers have played into the hands of the bull-party by buying considerable quantities at the beginning of the season, that is to say before the year 1912 was out. In our opinion the prices would not have risen as much as they have if the buyers, especially those in France, had bided their time, say until the beginning of 1913, before covering their requirements.

In view of the fact that the quantity now left over is very small, and that there is nothing else to fall back upon for the next six months, until the new crop comes in, any decline in the prices is out of the question, even if the orders to be executed should only be very small. For the rest it is sufficient to state that the average annual consumption of orris root equals about 690 tons, in order to make it clear that the 80 tons still available will not be sufficient to cover the requirements. It is generally said that the speculators will try gradually to force up the price of orris root within the next few months to 180 Lire, and possibly still higher, but only the future can show whether this scheme will succeed.

The fact that there is no root available in the country for the present season has induced a few of the producers and speculators to commence bargaining on a "grass basis" for orris root of the new crop. It is reported that a parity of 50 Lire grass basis has been paid, which is equivalent to a price for the root of from 150 to 160 Lire, according to the yield of the crop, in the producing district."

It will surprise no one who has carefully followed the course of the market that in the face of the conditions depicted above the prices of orris oil have risen considerably and that we have recently been again compelled to increase our quotations. The circumstance that the quantity still available is smaller than was the case in 1912, and that large parcels are held by speculators, appears to us to make any weakening of the prices within the next few months a matter of impossibility.

**Palmarosa Oil.** Since last autumn the market has remained almost without changes of any note. We hear that large transactions which were contemplated failed to end in business owing to the obstinacy of the Indian producers, who continued to stand out for high prices. As a result of this, somewhat considerable quantities have accumulated on the other side, and it is hardly likely that it will be possible to dispose of these without considerable sacrifices so long as consumers are able to avail themselves of our exquisite palmarosa oil substitute, a preparation which is well worth its price and which possesses nearly all the advantages of the natural oil. Our sales of this universally popular substitute have at times been so brisk that we have found ourselves compelled to refuse orders owing to lack of raw material.
Pastinac Oil. The circumstance that cases have repeatedly been reported of persons who had collected pastinac (Pastinaca sativa, L.) having contracted acute dermatitis of the hands\(^1\), has induced A. Nestler\(^2\) to make experiments upon his own person in the toxicity of the plant, as well as of the closely-allied Pastinaca opaca, Bernh., previous investigations into plants with an irritant action upon the skin having convinced him that he himself is highly sensitive to dermatic poisons. Nestler placed green leaves and parts of the stalks, as well as fruit of the plant upon sensitive places of both arms. He also rubbed his body vigorously with the hairy leaves and stalks. He further tried whether irritation could be produced with extracts with water, ether, chloroform, or alcohol, but in no instance was any effect observable.

Nestler was unable to discover the presence in the two pastinac species of any secreting organs which might exude a skin-irritating substance.

He regards it as not impossible that the cases of skin-affection after touching pastinac plants which have so far become known, are not in any way due to the plant itself, but may be caused by insects found on the plants, and he refers to the irritant properties of certain mites and caterpillars. He is of opinion that no skin-irritating action should be ascribed to pastinac until direct authentic experiments have proved it to possess this property.

Pennyroyal Oil. The reports to hand concerning the production in Algeria and in Spain are not unfavourable, and it has therefore been possible to buy at somewhat cheaper rates. But the quantities which are being offered are not large and it is therefore probable that the present prices will continue to rule. As already previously pointed out by us, however, the demand is very dragging.

Peppermint Oil, American. We are able to add to the information concerning American peppermint oil which appeared in our last Report the following particulars, which we have received from our New York friends: —

Speaking generally, the season of 1912 was in every respect disappointing. As already previously stated, a good crop was at first expected, and the prices slowly receded on account of the great extension of the area under peppermint. This applied specially to the western and northern districts of Michigan where, owing to the favourable condition of the snow, the plants had successfully weathered the winter of 1911—1912.

In other districts, however, the weather had been the reverse of favourable. In many places the fields were covered with ice, by which quantities of roots had been injured, with the result that the farmers were put to the greatest possible trouble in tyring to make good the damage by laying down new plantations, for it was taken for granted that the oil would realise high prices. As already stated, the result of this step was a very considerable extension of the plantations.

At the beginning of the summer of 1912 the position was still favourable, and in spite of heavy rainfalls which injuriously affected the crop, the results of the first weeks' distilling were fairly satisfactory. After this, however, prolonged spells of heavy rainfall ensued, in part attended by cloud-bursts, and within a brief period damage had been done representing a loss in oil of about 20,000 lbs. Thereupon the farmers who had suffered most began to spread exaggerated reports and the prices

\(^1\) Prof. Zinsser of Cologne, had called Nestler's attention to the fact that it had been found at Militz that persons who had collected pastinac for us had repeatedly suffered from acute dermatitis of the hands, and had been compelled to stop their work. — \(^2\) Berichte der deutsch. bot. Ges. 30 (1912), 581.
were rushed up comparatively quickly by operators who had covered their requirements in other peppermint districts, in order to make sure that they would be able to carry out the contracts for future delivery into which they had entered. Fundamentally there was no cause for such action, because the loss occasioned by the weather had been made good by the enlargement of the plantations, and in the upshot therefore the result of the crop was ample for the world's requirements. Fortunately the excitement was shortlived, and in view of the circumstance that two or three of the largest and financially strongest producers hold fairly considerable stocks, wherewith they are able to meet the needs of the market, we are likely to be spared surprises within the near future, but it does not appear impossible that prices will become still firmer, because the producers are naturally anxious not to lose money. But on the other hand they may find it impossible to dictate their own prices to the market, because so far as appearances go the New York dealers hold sufficient stock to cover the current requirements. There is no doubt that a certain proportion of 1912 oil will be carried over into the new season. The quality of last year's oil appears to have been fairly good everywhere, as the fields were on the whole free from weeds, but in any case it was not quite equal to that of the year before. This difference in quality is probably due to the severe showers which damaged the leaves and caused them to fall. As a result the peppermint, in many localities, showed a disproportionate amount of stalk in comparison with the leaf.

It would be too soon as yet to express an opinion on the prospects of the present year's crop, for as yet no reports have been received showing the condition of the plantations after the close of the winter. Our two brands "F. S. & Co." and "F. B." have been in exceptionally brisk demand during the winter, which shows that the care taken by our New York firm to buy for us none but the best oil which can be had, has been generally appreciated.

Peppermint Oil, English. During the winter-months trade in this article has been very quiet indeed at unchanged prices. Our London branch reports that in the opinion of its informants the market value of the oil is out of proportion to the unfavourable result of the last crop and that the only reason why the prices have been kept at such a comparatively low level was the competition of "cheap" Mitcham oils, which were being offered from all quarters. It is said that the stocks of really pure oil are very small indeed, and that such oils are firmly held at from 30/- to 31/- per lb. by a few financially strong dealers. On dry soil the plants are said to have stood the winter well, whereas the damp fields appear to have suffered somewhat considerable damage. The further development will of course depend entirely upon the weather-conditions of the next 3 or 4 months and it would be premature to forecast the result of the coming crop at the present time. This, however, is certain, that there is scarcely any chance of a fall in prices, for within the past two years very few new plantations have been laid down, and the production will therefore not be increased for the present. On the other hand the fact that the consumption of English peppermint oil on the Continent of Europe has fallen off considerably is of importance in considering the course of the market. This decline is due to the circumstance that in view of the keen competition in all peppermint preparations comparatively few manufacturers are able to afford the luxury of using such an expensive flavouring agent; the majority having recourse to American peppermint oil. The steadily increasing sale of our "F. S. & Co." brand, of which our New York firm is doing its utmost to perfect the quality, is a proof of this.
Peppermint Oil, Japanese. The market-position of the Japanese peppermint-products, and especially of menthol, has been extremely interesting last winter, but its interest has been equalled by the difficulty of forming an accurate view of the probable future of these articles, which are of such importance in our industry. The fact remains that the crop of 1912 has been a very good one, and that all the preliminary data for a reduction in the values to a normal level would have existed, were it not that the ordinary course of events was disturbed by speculative activity, which provoked conditions making it exceptionally difficult, if not impossible, to form a judgment of the true state of affairs. As was to be foreseen (and as we prophesied in our last Report), the spot-prices of recrystallised menthol rose towards the beginning of December to 90 ℳ, only to recede gradually to about 70 ℳ towards the end of the year and in January 1913. Throughout the period under review and at every price-level, business was extraordinarily animated, because there has perhaps never been a time when the ideas of the proper time for buying showed so much diversity. The only disturbing factor in the turnover was the occasional sagging of quotations down to 59 ℳ per kilo, but these movements were of course of a mere speculative character, and were mostly dictated by the universal stringency of money. As already stated, these were only passing incidents, and at the present time the quotations still revolve round the parity of 70 ℳ, although within the last few weeks trade has become decidedly duller. As we have said, it is impossible to foresee the future development of the market. On the one hand the fact must be taken into account that a considerable quantity of oil and crude menthol of the last crop is still awaiting shipment; on the other it must be borne in mind that, as already hinted, a financially strong English firm has recently judged it opportune to disturb the position by a speculative coup, and has taken a large quantity of crude oil (about 150,000 lbs.) out of the market. This action, as may be imagined, has caused a certain feeling of nervousness in the circles affected by it. So far as the future course of prices is concerned, it is an important question whether the principal consuming markets, Europe and the United States, are so well supplied with menthol that they are not under the necessity of covering any further requirements in Japan until the new crop is gathered, that is to say in July/August, or whether the available stock will not last until then. It is reported from several trustworthy sources that the good prices realised during the present peppermint oil season have induced the Japanese to extend their plantations, but it must be remembered that the success or failure of the plantations depends entirely upon the climatic conditions in the summer and autumn, and that it is therefore inadvisable to draw any conclusions as to the coming crop from this extension of the plantations.

Reports that the Japanese Government intended to monopolise the peppermint-production have proved to be unfounded.

Japanese peppermint oil, which for many years has been handled in Japan only in combination with crude menthol, has been much less affected than menthol by the important price-fluctuations which the last-named commodity has experienced during the winter. The stock of Japanese peppermint oil held in Europe is so considerable that the upward and downward movement of prices in Japan has hardly affected the selling-prices, and consequently the commercial oils prepared from the Japanese oil have remained unchanged in value.

From an official communication¹ we abstract the following table showing the value of the peppermint and peppermint oil produced in Japan during the last 10 years.

The value of the shipments of menthol is given on p. 104 of the same Annual as follows:—

<table>
<thead>
<tr>
<th>Year</th>
<th>Peppermint Yen</th>
<th>Oil Yen</th>
<th>Year</th>
<th>Peppermint Yen</th>
<th>Oil Yen</th>
</tr>
</thead>
<tbody>
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<td>1679831</td>
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</tr>
</tbody>
</table>

We abstract the following particulars on the Japanese peppermint oil industry from a report of the British commercial attaché at Yokohama which has appeared in the Board of Trade Journal\(^1\). Peppermint is cultivated in different parts of Japan, mostly on the hillsides, although that grown on low lying ground which can alternately be used for rice is richest in crystals. As the oil which has been freed from menthol crystals is inferior both in taste and odour to English and American oil, experiments have been made in the cultivation of English and American peppermint, but unfortunately without success. The best oil is produced in the districts of Okayama and Hiroshima, where three cuts are made yearly; in May, June, and August. The first cut yields about 47 p.c. of crystallised menthol\(^2\), the second about 53 p.c., and the third about 60 p.c. In the district of Yamagata only two, and in Hokkaido only one cut is made, but in the last-named district the area under cultivation is considerably larger than in the other, so that, in spite of a single crop and a crystallised-menthol-yield of only 45 p.c., more than one-half of the total output of menthol is produced in the province of Hokkaido.

The method of distilling is the same everywhere. It lasts four hours, the yield from 82 lbs. of dry leaf of the first cut being 14, of the second 24, and of the third 21 oz. of oil, or 1,07, 1,83 and 1,60 p.c. respectively. The value of course fluctuates, being dependent both upon the quality and the dryness of the leaves. The second cut is always the most prolific; thus, for example, a field which produces 300 lbs. of leaves in the first cut will yield 800 lbs. in the second and 600 lbs. in the third. The production per acre is about 5000 lbs. of dry leaves, yielding about 80 lbs. (≈ 1,60 p.c.) of oil.

The price of the leaves, like that of the oil, varies and the distillers only make small profits. The oil is collected by brokers, and resold to the large refineries, of which there are two of importance. In the districts of Odashitsuki, Okujoto, and Bingo there are so-called peppermint-guilds, who test the oil and give certificates of weight and purity. In the other districts the refiners must take the oil as it comes.

Menthol and dementholised oil are shipped in tins containing 5 lbs., twelve tins to a case. The United States import only menthol, but both products are shipped to other countries. In the year 1911 the exports of menthol amounted to 151,538 lbs. of the value of £ 98,300; those of oil to 229,800 lbs., value £ 63,900. The consumption

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1) *Board of Trade Journal* 79 (1912), 78. — 2) This refers exclusively to the menthol which is separated out from the crude oil by simple freezing without fractionation.
of menthol in Japan itself is not important (about 1500 lbs.), the principal buyers being the manufacturers of tooth-powders and patent-medicines. The oil is used in large quantities for cheap confectionery and the like.

We take this opportunity of referring to the detailed account of Japanese peppermint by Naojiro Inouye which is incorporated in our Report of November 1908 (pp. 199 to 233).

\textit{d-Ethyl-n-amylcarbinol}, the occurrence of which in Japanese peppermint oil we mentioned in our Report of April 1912, p. 102, has since then been prepared by us synthetically. We started from \textit{n-caproic} aldehyde prepared by the familiar method. The aldehyde, which was purified from the primarily-produced bisulphite-compound, constitutes a very mobile liquid with a slightly acrid odour, b. p. 35 to 37° (19 to 20 mm.); \(d_{150} 0,8185\); \(n_{D20} 1,42785\). We found the m. p. of the semicarbazone to be 114,5 to 115,5°, whereas according to P. Bagard\(^1\) it is 106°. We reacted upon the caproic aldehyde with magnesium ethylidode and thus obtained \textit{i-ethyl-n-amylcarbinol}, of which the properties are set forth in the subjoined table:

\begin{align*}
\text{i-Ethyl-n-amylcarbinol} & \quad \text{d-Ethyl-n-amylcarbinol} \\
\text{(synthet.)} & \quad \text{(from peppermint oil)} \\
\text{B. p. 176 to 177,5°} & \quad 178,5 \text{ to 179,5°} \\
\text{\(d_{150} 0,8286\)} & \quad \text{0,8276 to 0,8279} \\
\text{\(n_{D20} 1,42785\)} & \quad \text{1,42755 to 1,42775} \\
\text{\(n_{D150} 1,42975\)} & \quad \text{65,5 to 66°} \\
\text{Mol. Refr. 40,55, calc. f. C\textsubscript{8}H\textsubscript{18}O 40,67} & \text{Acid phthalate, m. p. 65 to 65,5°} \\
\text{Calc. for C\textsubscript{8}H\textsubscript{18}O 40,67} & \text{65,5 to 66°}
\end{align*}

The acid phthalate of \textit{i-ethyl-n-amylcarbinol}, re-dissolved from chloroform, when mixed with the same ester of the natural alcohol, suffered no depression of m. p. Sap. v. 61,1; calc. for C\textsubscript{8}H\textsubscript{18}O\cdot\text{CO}_{2}\cdot\text{C}_{8}\text{H}_{17} 60,5.

From the natural \textit{d-ethyl-n-amylcarbinol}, we prepared the benzoate. This constituted a somewhat viscous, colourless liquid, with a faint odour; b. p. 126,5° (3 mm.); \(d_{150} 0,9641\); \(\alpha_{D} + 5° 58\); \(n_{D20} 1,48905\); ester v. 240,8 and 239,6 = 100,5 and 100 p. c. octyl benzoate. The acetate was formed when \textit{d-ethyl-n-amylcarbinol} was boiled with acetic anhydride and anhydrous sodium acetate. It constitutes a liquid with a peculiar odour, at the same time fruity and reminding of rose oil: b. p. 194 to 194,5°, \(d_{150} 0,8693\), \(\alpha_{D} - 4° 46\), \(n_{D20} 1,41535\), ester v. 327,5 and 328,5 = 100,8 and 100,5 p. c. octylacetate. It is a curious fact that the dextrorotatory alcohol yielded a laevorotatory acetate. The alcohol regenerated from the laevorotatory acetate, showed almost the same degree of dextrotorsion (\(\alpha_{D} + 6° 20' [-3° 10' in a 50 mm. tube]) as the original (\(\alpha_{D} + 6° 37'\)).

We have also repeated the process (already referred to in our last April Report) of oxidising natural \textit{d-ethyl-n-amylcarbinol}, and obtained \textit{n-caproic} acid, b. p. 77,5 to 80° (3 mm.), \(d_{150} 0,9342\), acid v. 484,5 = 100,25 p. c. caproic acid. Analysis of the silver-salt: found 48,60 p. c. silver, calc. for C\textsubscript{8}H\textsubscript{11}AgO\textsubscript{2} 48,43 p. c. The amide gave m. p. 100 to 100,5° (from water) which is characteristic of \textit{n-caproic} amide.

Two years ago we mentioned in our Reports\(^3\) the experiments which have been made by Thoms in the cultivation of Japanese peppermint at Dahlem, near Berlin, and

\(^{1}\) According to A. Lieben and G. Janecek \textit{Liebigs Annalen} 187 (1877), 131 the density is \(d_{200} 0,8335\); but the estimation of these authors, as they themselves acknowledge, is not quite reliable because the aldehyde was probably already oxidised in part. — \(^{2}\) \textit{Bull. Soc. chim. IV.} 1 (1907), 319. — \(^{3}\) Report April 1911, 92; October 1911, 71.
we stated that at his suggestion similar experiments had been made elsewhere, for instance in German South West Africa. Thoms had obtained the plants through the intermediary of one of his Japanese students from a farmer in Yamagata-Ken. The distinguished authority on the Mentha-species, Briquet, of Geneva, had undertaken the botanical examination of the plants, and had pronounced Mentha canadensis var. piperascens, Briq. to be the parent-plant. Briquet supposes that the species is identical with that which had been identified by Holmes as Mentha arvensis DC. var. piperascens, Holmes.

The accuracy of Briquet's view is doubted in an article on Japanese peppermint oils which appears in an English journal¹). It is here suggested that two different species are in question. The plant which was examined by Holmes, and at the same time by the French botanist Maluivaud was recognised by both without doubt as being a variety of Mentha arvensis, and showed well-marked differences from the species examined by Briquet. This plant had been introduced into Europe from Japan by Thomas Christy towards the end of the 'eighties and had been grown in Sydenham and at Sevenoaks. An oil distilled from these plants in the year 1888 was obviously deficient in menthol, for even when the bottle was placed in ice no menthol crystallised out. As on the other hand the peppermint oil distilled by Thoms was very rich in menthol, this would seem to afford a further proof that the two plants were different.

We merely reproduce here the views of the English author and will only, in addition, quote from his article the statement that Chinese peppermint oil, to which we have also made reference in previous Reports (October 1910, 96) is probably the product of Mentha canadensis var. glabrata, of Prof. Arthur Gray.

**Pimento Oil** has remained unaltered. There have been ample opportunities for acquiring distilling material at reasonable rates, and there has therefore been no lack of oil. There have been no changes in the price.

**Pine-needle Oils.** The sphere of employment of Siberian pine-needle oil, an article of which we import enormous quantities, is extending from year to year, for the reason that its moderate price has given it a footing in the manufacture of an exceptionally wide range of technical articles, such as disinfectants, boot-polishes, lubricants, artificial turpentine oils, lacquers, &c. Unfortunately business has been seriously impeded by price-cutting on the part of certain firms. The parcels in which price-cutting took place were mostly consignments which had to be sold at almost any price they would fetch, and which partly proved to be doctored to a considerable extent with pine-tar oil. There has been a very sustained demand for our oil, of which the quality is subject to stringent control, and as for the present there is no over-production in oil of this grade there is no prospect of any reduction in prices in the near future.

The advance in prices of oil of Pinus Pumilio which we prognosticated in our last Report has in the meantime actually taken place, one of the leading producers in Lower Austria having retired from the market, and the call upon the other factories having consequently become much greater. So far there is no further news concerning the new source of production in Transylvania to which reference was made in our Report, but we hear that preparations have latterly been made in Galicia for exploiting the extensive Pumilio pine areas in that country. It is therefore to be expected that the shortage caused by the retirement of the Lower Austrian manufacturer will be

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¹) Perfum. and Essent. Oil Record 4 (1913), 32.
made good quite soon, but all the same we do not anticipate that prices will again be reduced on that account.

Pine-needle oil from *Abies pectinata*, which on account of its fine odour plays a prominent part in the manufacture of "air purifiers", used as sprays in dwelling-houses, has been available in sufficient quantities, although we understand that its production in the forest-areas of Lower Austria is on the decrease. Oil from the cones of *Abies pectinata* (*Ol. temtinum*) has only been offered in very moderate quantities, but the supplies are not out of proportion to the demand, and consequently there has been no occasion for any alterations in the price.

**Oil of Primula officinalis.** Some years ago we referred to an investigation conducted by A. Goris and M. Mascré\(^1\), according to which the root of the primrose species, *Primula officinalis*, Jacq., contains the glucosides primverin and primulaverin, as well as the ferment primverse. The authors, in collaboration with C. Vischniac\(^2\), have continued their investigations and have obtained the interesting results set forth below. The best method of isolating the glucosides from the root is as follows: for the purpose of destroying the ferment contained in them, the roots are first placed in an autoclave and exposed to the action of alcohol-vapour at 105 to 110° for from 5 to 10 minutes. Having thus been "stabilised" the root is powdered and treated with boiling acetone in the presence of calcium carbonate. The acetone-extract is then evaporated, the residue dissolved in water and the aqueous solution shaken with ether until the latter has ceased to acquire colour. The water is evaporated *in vacuo* and the residue treated with a mixture of 9 parts anhydrous acetic ester and 10 parts 95 p.c. alcohol. The greater part of the glucosides is dissolved out by this manipulation. The residual portions of the extract may again be extracted with alcoholic acetic ester after being treated with acetate of lead, further quantities of the glucosides being obtained by this method. The authors succeeded in separating the two glucosides by means of repeated successive washings-out with 95 p.c. alcohol and anhydrous acetic ester. The average yield of 1000 grams of green root was 1 gram = 0,1 p. c. of crude glucoside-mixture. From this mixture they were able to isolate from 20 to 25 p. c. primverin and from 10 to 15 p. c. primulaverin. The rest consists of intermediary products, with the complete resolution of which the authors have not occupied themselves up to the present. The extraction is incomplete, inasmuch as the essential-oil yield of the green root is 0,08 p. c., which corresponds to 0,2 p. c. of glucosides.

The root of *Primula Kewensis*, Hort., compared with the green substance, yielded 0,2 p. c. glucosides of identical properties with those of the first-named species.

Primverin is a glucoside \(C_{20}H_{28}O_{13}\), forming anhydrous crystals, and liquefying at 203 to 204° on the Bloc Maquenne, with a corresponding m. p. of 206°. \([\alpha]_D = 71,53°.\) The previously given characters, *viz.*, m. p. 172°, \([\alpha]_D = 60,24° are incorrect, but the small quantity of experimental material available at the time when these data were given precluded any thoroughgoing separation. When hydrolysed with acids 1 molecule of primverin yields 2 molecules of monoses and 1 molecule of \(\beta\)-methyl-\(\beta\)-methyl-resorcylate. It was impossible further to identify the monoses; they occur in the primverin molecule in the form of a biose, which splits up when treated with acid. The biose can only be split off from the glucoside by biological treatment, with the aid of primverase. It is as yet unknown, and has been called primvero by the authors. The two monoses referred to above are probably a pentose and a hexose.

The principal constituent of the essential oil of primula root is \( p \)-methylether-\( \beta \)-methylresorcylic (4-methoxy methyl salicylate). It melts at 49° and is identical with the so-called primula-camphor\(^1\)). Its constitution was ascertained by combustion and by saponification into \( p \)-methylether-\( \beta \)-resorcylic acid (4-methoxy salicylic acid), m.p. 158 to 159°. The acid was identical with the product described by Tiemann and Parrisius\(^2\)). The constitution of \( p \)-methyl ether-\( \beta \)-resorcylic acid was further ascertained by demethylation with hydriodic acid and subsequent splitting-off of carbonic acid. The result was resorcinol.

The following equations show the decomposition of primverin by means of fermentation and of acids respectively:

I. Decomposition by fermentation:

\[
\begin{align*}
\text{Primverin} & \rightarrow \text{Primrose} \\
\text{COOCH}_3 + \text{OCH}_3 & \rightarrow \text{COOCH}_3^{(1)} + \text{OCH}_3^{(4)}
\end{align*}
\]

II. Decomposition by acids:

\[
\begin{align*}
\text{Primverin} + 2\text{H}_2\text{O} & = \text{C}_6\text{H}_5\text{O}_5 + \text{C}_6\text{H}_{10}\text{O}_6 + p\text{-methylether-}\beta\text{-methylresorcylate}.
\end{align*}
\]

By the name of primulaverin the authors designate a body with m.p. 161 to 163°, \( \alpha_p = 66,56° \). It crystallises with 2 molecules of water and possesses the same empirical formula as does primverin. It probably results from an isomorphous crystallisation of primverin with primulaverin proper, which latter up to the present has not been isolated in the pure state and which appears to be closely related to primverin. The essential oil which is formed from primulaverin by hydrolysis consists of a mixture of the methyl esters of \( p \)-methylether-\( \beta \)-resorcylic acid and \( m \)-methoxy salicylic acid.

It was now an easy matter to ascertain the constitution of the essential oil which is obtained by the steam-distillation of primula root. A quantity of 40 grams of green root was carefully ground up and macerated with water for 24 to 28 hours. In the process of distillation the mass effervesced strongly. 8,56 grams = 0,0214 p.c. of scales with a mother-of-pearl like lustre passed over, while the distillation water was found to contain 26 grams = 0,065 p.c. of a mass consisting to the extent of about 75 p.c. of solid matter. The total yield was 0,0864 p.c. The solid mass crystallises from dilute alcohol in needles, m.p. 49 to 51°. The highly-diluted solution has a clearly-perceptible odour of Russian anise; when more highly concentrated its odour reminds first of the cinnamate, and afterwards of the salicylate of methyl- and benzyl-alcohol. When saponified, the solid substance yielded \( p \)-methylather-\( \beta \)-resorcylic acid (m.p. 158°); while the saponified liquid portions yielded chiefly \( m \)-methoxy salicylic acid (m.p. 142 to 143°).

With the object of preparing the essential oil of the flowers, water was first poured over the latter, and after 6 hours they were distilled, yielding 0,00686 p.c. of a pale green oil. The distillation-water contained 0,00826 p.c. oil. The oil consists in part of saponifiable and in part of non-saponifiable constituents. The former again yielded \( p \)-methylether-\( \beta \)-resorcylic acid and \( m \)-methoxy salicylic acid. So far the constitution of the non-saponifiable constituents has not yet been ascertained.

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The authors have as yet been unable to decide whether primverase is or is not a new ferment. It is without doubt closely allied to, if not identical with, betulase, which occurs in Betula lenta, Gaultheria procumbens, and Monotropa Hypopithys. The ferment powder is obtained from the dried leaves of the calyx, the glucosides being removed by extracting with alcohol and ether and the ferment being thus left behind in the powdered leaves. Emulsin, invertin, the ferment of Aspergilus, and myrosin do not react with the primula glucosides. On the other hand, hydrolytic decomposition occurs with the ferments from Monotropa Hypopithys, Betula lenta, and Gaultheria procumbens which are obtained by the method described for primverase.

It is scarcely possible to give a definite answer to the question how the ferment is distributed within the primula plant. In the root it is found chiefly in the tap-root; in the parts above ground it occurs principally in the neighbourhood of the outer vascular system, that is to say in the epidermic cells of the calyx, especially of the petals. The glucosides are distributed throughout all parts of the plant.

The ferment primverase is found widely distributed throughout the family of the Primulaceae. It has been detected in Primula elatior, P. Auricula, L., Samolus Valerandi, L., Lysimachia vulgaris, L., L. nemorum, L., L. nummularia, L., Anagallis arvensis, L., Hottonia palustris, L., Dodecatheon Meodia, L., Glauk maritima, L., and Cyclamen latifolium Sibth. et Sm. The plants do not always contain the glucosides as well as the ferment.

Not all the green roots of the Primula, when triturated in a mortar, give off an odour of anise like those of Primula officinalis. But an aqueous solution of the extracts invariably gives the characteristic colour-reaction with ferric chloride.


The following develop an odour of methyl- or amyl-salicylate: Primula longiflora, All., P. frondosa, Janka, P. grandiflora, Lam., P. acaulis, Hill., P. cortusuoides, L., P. obconica, Hance, and P. elatior, Hill.

An odour of coriander is given off by Primula Auricula, L., P. pannonica, A. Kern and P. Palinuri, Petagn.

With Primula involucrata, Wall., no odour was observable. Lysimachia nemorum, L. gave a faint odour of methyl salicylate, while the roots of Dodecatheon Meodia, L., when triturated, develop an odour reminding of anise, and those of Anagallis arvensis, L., an odour reminding of valerian.

Oil of Rhus Cotinus. Under the name of "Essence de Fustet", a small sample of oil from the leaves and flowers of Rhus Cotinus, L., N. O. Anacardiaeces, was recently sent to us. The parent plant of this oil is the so-called Zante fustic to which we have already briefly referred in our April Report of 1910, p. 92. The faintly palish yellow, almost colourless oil had the not very characteristic odour of the terpenes; perhaps reminding slightly of neroli. The small quantity at our disposal only allowed of a superficial examination. The oil was found to possess the following constants: d_{150} 0.8710, α_{D} +32° 54', n_{D20} 1.4887, acid v. 0.9, ester v. 20.4, sol. in 6 vols. a. m. 90 p.c. alcohol.

Distillation showed the oil to consist almost entirely of terpenes. When the lowest-boiling fraction, b. p. 161 to 164° (d_{150} 0.8563) was tested for camphene with glacial acetic-sulphuric acid, it afforded isobornylacetate, which upon saponification yielded isoborneol. β-pinene could not be traced with certainty in the fraction boiling
between 164 and 167°. However, oxidation with alkaline permanganate gave rise to lustrous leaflets of a sparingly-soluble sodium salt, perhaps sodium-nopinate. The oil which passed over between 170 and 174° contained no phellandrene. On the other hand, a fraction with b. p. 174 to 176° (d_150^0 0.8454; α_D^0 + 54° 40') contained limonene, as was shown by the formation of limonene tetrabromide, m. p. 103 to 104°, when brominated in glacial acetic acid solution. The same fraction, when saturated with hydrochloric acid gas under cooling, gave dipentene dihydrochloride, m. p. 50°. With dipentene dihydrochloride of different origin this derivative suffered no depression of m. p. The fractions of the oil which were the last to pass over, b. p. 177 to 179° (d_150^0 0.8429; α_D^0 + 63° 50'), were tested for terpinene with negative results.

Rose Oil, Bulgarian. Trade in this important article has been thoroughly unsatisfactory throughout the past winter, inasmuch as consumers were very rightly most averse from conceeding the enormous prices demanded for first-class quality. Our offers are in an increasing degree met with the objection: "we are able to buy a guaranteed pure oil, which answers all the tests, at several 100 marks per kilo less money". It is unnecessary for us to express an opinion of the peculiarities of these cheap qualities, but it is in the highest degree regrettable that even old-established firms with honoured names should lend themselves to the traffic in such merchandise, although from their relations with the sources of supply they must be thoroughly conversant with the cost of really pure oil. As the result of the war has been favourable for Bulgaria, the hostilities have not contributed to raise the price of rose oil; on the contrary, holders showed themselves disposed at times to make concessions in order to obtain ready money. Up to the present little can be said as to the prospects of this year's crop, the climatic conditions of the next few months being the determining factor in the development of the flowers. One of our correspondents informs us that the rather warm weather which prevailed towards the end of January has brought the new shoots forward somewhat precociously, but that afterwards a few severe frosts have done considerable damage, and that for this reason it may be necessary to prepare for another poor harvest. Owing to the war it has been difficult to procure any statistical data; we hope to be able to give further particulars in our next Report.

The following report 1) from another source has also reached us:

The crop of 1912 was one of the smallest since 1871, its total output having reached only 2987 kilos, which, compared with the crop of 1911, shows a falling-off of about 30 p. c. It has nevertheless been one of the most profitable crops on record. The average price of flowers until the year 1910 was 20 centimes per kilo, whereas the average price of flowers in the season 1912 was 45 centimes per kilo. The total output of flowers of the 1912 crop amounted to about 9 000 000 kilos, with an average yield of 1 kilo of rose oil per 3000 kilos flowers. In 1912 the average price of rose-oil has also been the highest ever known, that is to say 2520 Fr. per kilo; whereas the average price during the period from 1880 to 1910 was only 1020 Fr. per kilo. So high an average price as that of the season 1912 is seemingly abnormal, but the advance was almost inevitable. In the course of the last five years everything has doubled, or even trebled in price in Bulgaria; the consumption of oil of rose has more than doubled since the year 1900, and since 1901 the crops have fallen below the average demand. The stock of rose oil in the growing districts is entirely exhausted,

1) Dated April 12.
the available supplies are exclusively in the hands of the exporters, and these supplies cannot exceed from 300 to 400 kilos. As a result of the Balkan War the demand for rose oil has been very sustained, and all the more recent sales in Bulgaria have been made at prices varying from 2600 Fr. to 3400 Fr. per kilo.

As regards the new crop, the general prospects are not very encouraging. Almost everywhere, and especially in the low-lying gardens, the rose trees do not look very hardy, and present a more or less enfeebled appearance. This is probably due to mildew and other diseases from which they have been suffering for the past three years, to the scanty and intermittent care they have lately received owing to the war, and especially to the recent frosts. All this damage, however, may easily be made good if the weather is favourable during the month of April and especially during the distilling season. At present the weather remains chilly. It is still too early to forecast the result of the next crop, but the output is expected to be not less than a middling one, and no reduction in the price of rose oil is looked for, the more so because there is no old stock left, and because the opening price of the flowers of the new crop is already 30 p. c. above that of last season.

Among the samples of rose oil which have been submitted to us for our opinion in the course of the past six months several proved to be adulterated with spirit. We need not refer in detail here to this form of adulteration, because it has already been discussed repeatedly in our Reports. We wish, however, specially to mention in this place an oil which was not only adulterated with spirit but also in another fashion, namely with artificial ester. That the sample was adulterated was already evident from its constants, which were in part wholly abnormal: \(d_{300} 0.8976, \alpha_p - 0.57^\circ, n_{D30} 1.45842,\) sol. p. +24\(^\circ\), acid v. 7.3, ester v. 172.1 = 60.2 p. c. ester calc. as geranyl acetate, ester v. after acet. 271.3 = 93.7 p. c., calc. as total geraniol.

Apart from the fact that in this sample the sp. gr., acid value and percentage of total esters are much too high, the abnormal ester value is particularly noteworthy, seeing that in commercial oils of good quality this value ranges from 7 to 16 p. c. Our suspicion that an artificial ester had been added to the oil was confirmed by further examination, which showed the corresponding acid to be probably phthalic acid, as appears to be indicated among other reasons by the fact that when it was melted with resorcinol and zinc chloride fluoresceine was generated. The acid was probably present in the oil in the form of ethyl phthalate, but owing to lack of sufficient experimental material it was impossible to decide this point. Judging from the ester value the addition amounted to about 30 p. c. We were also able to detect about 6 p. c. of spirit in the oil.

J. C. Umney\(^1\) has utilised the colour test recommended by Dodge and Olcott for the detection of gurjun balsam in order to detect the presence of the oil of gurjun balsam in rose oil. To 5 drops of the rose oil under examination, Umney added 10 cc. of glacial acetic acid and 3 drops of pure nitric acid and shook the mixture well. A reddish-violet colour developing in about 30 seconds indicates the presence of gurjun balsam oil, and according to Umney this test makes it possible to detect so small a proportion as 0.5 p. c. of the adulterant in rose oil.

In our Report of April 1912, p. 108, we had called attention to the adulteration of rose oil with gurjun balsam; an adulteration which had not previously been observed. We gave exact chemical proof of the presence of gurjun oil by oxidising a strongly-

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\(^1\) Per\(f\)um. and Ess\(e\)nt. Oil Record 3 (1912), 287, 291.
active fraction of the suspect oil (b. p. 255 to 262°) with potassium permanganate in acetone solution and treating the oxidation-product with semicarbazide. The result was a semicarbazone, m. p. 234°, which was completely identical with that obtained from gurjun balsam oil by a similar method.

As this semicarbazone, as shown by Deussen and Philipp, is characteristic of gurjun balsam oil, the occurrence of the last-named substance in the rose oil under examination had been proved by us beyond the possibility of doubt. Umney, however, still appears to question this, unless he has misunderstood what we stated on the subject at the time, for in the article quoted above he declares, referring to the rose oil examined by us, that we had found it to contain a strongly laevorotatory oil, "which in our opinion was possibly the oil of gurjun balsam." We feel bound to enter an energetic protest against such a distortion of the facts. Our chemical examination left no doubt whatever of the nature of the adulteration, and this we expressed in our Report without any ambiguity, as any unbiased reader of our article will readily admit.

In our examination we deliberately refrained from colour-tests, because what we were concerned with was the actual detection of gurjun oil, and because a colour-test is always a last resource, with which the investigator willingly dispenses when he has better methods at command. In applying the test recommended by Umney we were unable to detect an addition to rose oil of even 5 p. c. of gurjun balsam oil, hence, for the purpose under discussion, this test is worthless, in spite of which Umney proudly calls it "a positive clue"!

P. Siedler, in a lecture, has given an account of the growing of roses and the manufacture of rose oil in Bulgaria, which is of additional interest because the lecturer himself has thoroughly studied the gathering of the flowers and the distillation of the oil on the spot in the months of May and June 1912, and because expert reports on this subject are rarely obtainable from this somewhat inaccessible district.

Kazanlik, which is generally considered to be the centre of the rose-cultivation, is no longer the principal distilling-point, although it may be described as the chief seat of the trade in rose oil. The harvest begins a little later in Kazanlik than in the Gropsu Valley (Gjöbsu) which is situated a little further West, and in the first-named place it had not yet begun at the commencement of June. The copper stills which are used throughout the region by those peasants who do not simply content themselves with rose-growing, were at that time being made and mended in the streets of Kazanlik.

In Karlovo, on the other hand, the distilling was already in full swing. Here the rose oil is prepared in small distilling sheds by the old method, which remains in general use to this day. Many people work in outhouses close to their dwellings. These outhouses are built for the purpose and are kept closed; a few large firms however possess works which are equipped on modern lines.

Broadly speaking, about 3000 kilos of roses are required to yield 1 kilo of oil; the average weight of the flowers is 400 to the kilo; about 30 roses are needed to produce one drop of oil. Apart from the conditions of labour, the oil-yield depends in the first place upon the weather, more oil being produced when the weather is cool and the sky covered than in good weather, because the hot Bulgarian summer-

sun causes the oil to evaporate readily from the cells. The output also depends upon the species of roses grown. The white rose, called güll in Bulgarian, is a variety of *Rosa moschata*, Mill. It produces about half as much oil as does the red rose (*tcherwen güll* in Bulgarian) of *Rosa damascena*, Mill., and the oil of the last-named is poorer in stearoptene than that of the white rose. But the white rose has the advantage of growing in places where the red rose does not flourish so that, in spite of its poor oil-yield, it is still largely cultivated. For distilling, a mixture of white and red roses is generally taken. A certain constancy is observable in the oil produced in each different district. After being freed from the oil the distillate constitutes a special article of commerce in the form of concentrated rose-water, which is used for cosmetic as well as for culinary purposes and also in preparing rose-liqueur.

At the present time the chief rose growing centre is Rahmanlari (Rasmanlaro). At harvest-time the whole neighbourhood of this place resembles a flowering garden. From 600,000 to 700,000 kilos of roses are distilled here every year, and here it is that the cultivation of the roses can best be studied.

There are various methods of propagation. When a garden has grown too old the bushes are cut down in the autumn, the roots are divided up, planted in furrows which are drawn from 1½ to 2 yards apart, and covered with earth and manure. Every cutting, of course, must have eyes. Another method of propagation is by layering. The first flowers appear in the second year and thence onward the yield of the plantations increases until the tenth year, when the bushes are cut down and begin to sprout again. It is necessary to remove the dry wood carefully every year and burn it, so that the new shoots may have air and the spores of the fungi in the dry wood may be killed off. Shortly before the flowering the beds are cleaned with a wooden plough or with a hoe, and the plants trenched, with the result that ultimately the rose-bushes occupy the high side of the bed. The older the plantation, the less, in the end, grows the output, but when carefully tended a plantation may reach a great age. The Bulgarian rose has the virtue of being a remarkably free-flowering plant, and the regularity of its flowering is very interesting, the buds on a stalk always numbering 1, 3, 5, 7, 9, 14, 21, or 28. Intermediate numbers, it is said, do not occur.

When the flowers are gathered they are broken off immediately below the calyx, which is easily done in the case of the Bulgarian rose. They are then taken as quickly as possible to the place of distillation in baskets or wooden tubs, in order to obviate loss by fermentation. During the gathering a little flower-wax accumulates at the fingers of the women who collect the flowers. This is scraped off and is used in the preparation of an eye-ointment, for scenting tobacco, and for coating the metal necklaces of the girls.

The chemical constitution of the oil depends upon the species of the flower and the district where it is grown. The oil produced in the elevated Balkan-villages contains the greatest proportion of stearoptene, about 15 p.c.¹), while that of the plains contains only about 10 p.c. The aroma of the oils of different districts also varies to a not inconsiderable extent. The villages in the extreme East of the district of Nova-Zagora produce an oil of which the density is sometimes as low as 0,840, while the solidifying-point²) goes up to +21°. The oils of the district of Karlovo have a solidifying-point of 17,5 to 20° and a sp. gr. of 0,853 to 0,858. But as the dealers

¹) We have found good commercial oils to contain up to 20,6 p.c. stearoptene. — ²) Siedler very aptly, in the case of rose oil, refers to the solidifying-point as "crystallisation-point."
mix the oil which they themselves prepare with that supplied to them by the growers, a uniform product of the same condition is obtained, which answers the requirements. Bulgarian dealers of repute are endeavouring to protect themselves against adulteration by establishing in the chief oil-producing localities small works where they themselves distil some oil, in order to obtain thereby a guide to the natural characteristics of the oil of the locality for comparison with that offered to them by the peasants. With the adulterants in use we have repeatedly dealt in our Reports.

**Rosemary Oil.** Generally speaking, the sale of French rosemary oil has left very much to be desired, although we have no lack of customers for our quality of oil, which is equal to the highest requirements. It is regrettable that certain firms of middlemen indulge freely in malpractices in their dealings in the article, "cheap" offers of highly adulterated quality, which entice buyers solely on account of their low price, being the order of the day. The cheap Spanish oils also, with their abnormal chemical and physical properties, made business in pure oil extraordinarily difficult. Only too often we are met with the objection that the cheap quality is good enough and that the buyer is unable to pay the price of our oil. In such cases it is our practice to point out that the most advantageous way of procuring such cheap oils is for the consumer himself to mix pure oil with the well-known adulterants. Unfortunately large numbers of the consumers regard this as a job of which the trouble is out of proportion to the gain. There has been a somewhat brisker demand for Dalmatian rosemary oil, the value of which has therefore been maintained. We have shipped considerable quantities of this oil to the United States where, we are glad to say, its characteristic properties continue to be much appreciated.

**Rue Oil.** Our correspondents send us somewhat more favourable reports of this article. The distilling season in Algeria is again approaching its close, but the prices have not yet given way to such an extent that we would feel justified in reducing our quotations at this moment. We again wish to point out that our tests for quality are extremely stringent and that the only grade of oil sold by us is that which completely solidifies at +8°.

For the quantitative estimation of ketones in oil of rue, comp. p. 45.

On the conversion of the methylnonyl ketone of oil of rue into undecane, see p. 141.

**Sandalwood Oil, East Indian.** The further important upward movement in the prices of sandalwood will have caused no particular surprise to our readers, seeing that we have not omitted to give hints of the impending advance. A large proportion of our regular customers have thus been enabled to cover their requirements in good time and will in all probability have cause for satisfaction with their contracts. At the auctions, of which particulars are given in the tables on pp. 92 and 93, the demand which manifested itself caused an immediate increase in prices of about 25 p.c., which developed, in the course of the sales, to a rise of 100 p.c. It is said that the first impetus towards this rise came from the Indian buyers, but on the part of European buyers also a certain feeling of nervousness was apparent. Who knows whether, with a little more circumspection, events would not have taken a different course? Sandalwood oil gradually advanced to about 45 sh., and even at this price, which had never been known before, business was quite brisk. Nor has the general tendency been
<table>
<thead>
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<th>Tons</th>
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<td>Hunsur 16/12 1911</td>
<td>Seringapatam 18/12 1911</td>
<td>Bangalore 13/12 1911</td>
<td>Hassan 21/11 1911</td>
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<td>54/9 62/6</td>
<td>— 69/101/2</td>
<td>54/— 82/6</td>
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<td>52/3 59/71/2</td>
<td>51/9 64/—</td>
<td>50/9 73/—</td>
<td>50/6 82/3</td>
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<td>— 61/9</td>
<td>— —</td>
<td>— —</td>
<td>— 83/6</td>
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<tr>
<td>1st Class Roots</td>
<td>— 62/3</td>
<td>— 66/3</td>
<td>69/3 81/3</td>
<td>54/6 84/6</td>
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<td>— 69/6</td>
<td>68/6 82/3</td>
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<td>3rd &quot; &quot;</td>
<td>— 61/—</td>
<td>— 68/6</td>
<td>— 74/3</td>
<td>— 79/3</td>
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<tr>
<td>1st &quot; Jugpokal.</td>
<td>51/9 59/9 to 60/9</td>
<td>51/9 61/9 to 67/3</td>
<td>50/3 66/3</td>
<td>49/6 81/—</td>
<td>49/— 82/6</td>
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<tr>
<td>2nd &quot; &quot;</td>
<td>— 59/71/2</td>
<td>51/— 59/9 to 60/11/2</td>
<td>49/6 65/3</td>
<td>49/— 81/9</td>
<td>48/3 82/3</td>
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<tr>
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<td>— 58/41/2</td>
<td>— 60/—</td>
<td>— 66/—</td>
<td>— 47/—</td>
<td>— 81/—</td>
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<tr>
<td>Cheria</td>
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<tr>
<td>Ain Chilta</td>
<td>— 46/9</td>
<td>36/— 48/3</td>
<td>47/— 52/6</td>
<td>59/— 59/—</td>
<td>33/6 60/— to 30/9 62/3</td>
</tr>
<tr>
<td>Hatri Chilta</td>
<td>— 31/3 36/9</td>
<td>31/3 37/—</td>
<td>29/6 39/— 29/6 46/—</td>
<td>28/6 49/41/2</td>
<td>27/6 51/9 26/3 58/3</td>
</tr>
<tr>
<td>Milwa Chilta</td>
<td>26/— 32/—</td>
<td>26/— 29/9</td>
<td>23/9 31/3 23/— 43/—</td>
<td>22/9 44/101/2</td>
<td>22/6 42/3</td>
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<tr>
<td>Basola Bukni</td>
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</table>
greatly affected by the circumstance that later on, especially at the turn of the year, there were numerous second-hand offers at lower prices, mostly on the part of firms which had cheap contracts still running, which were not over-confident in the future of the market, or which were compelled to sell owing to the general tightness of money. For our part, we take by no means an optimistic view of the situation; on the contrary, we feel convinced that for the present there is no chance whatever of any reduction in prices. The larger are the quantities of dear wood from the auctions which are placed upon the market, the higher will go the quotations for sandalwood oil, seeing that the low-priced wood from previous years' auctions has been used up as a result of the brisk turnover of last autumn. Part of the time our unique distilling-plant has been running day and night in order to turn out the large quantities of oil which we supply to the principal buyers at home and abroad. It is well known that we pay particular attention to the manufacture of an extra quality containing 94 p.c. santalol.

Those of our readers who are not in close touch with the trade in sandalwood oil will be interested in the subjoined table showing the price of pure East Indian oil during the last 10 years:

<table>
<thead>
<tr>
<th></th>
<th>March 15th 1904</th>
<th>March 15th 1909</th>
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<tbody>
<tr>
<td></td>
<td>Rs. 22.-</td>
<td>Rs. 23.-</td>
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<tr>
<td>15th 1905</td>
<td>24.-</td>
<td>15th 1910</td>
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<td>15th 1906</td>
<td>24.-</td>
<td>15th 1911</td>
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<tr>
<td>15th 1907</td>
<td>24.50</td>
<td>15th 1912</td>
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<tr>
<td>15th 1908</td>
<td>24.50</td>
<td>15th 1913</td>
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</tbody>
</table>

From the report of the Conservator of Forests in Mysore to his Government, which naturally reflects great satisfaction with the result of the auctions, we take the following particulars relating to the season 1911:

The total quantity of 2348 tons 1 cwt. 94 lbs., that is to say 143 tons more than in the previous year, realised Rs. 1254155-5-1, or R. 218742-7-3 more than in 1910. The average price realised for the wood was Rs. 534, as compared with Rs. 471 in the year 1910 and Rs. 455 in the last 10 years.

J. Pohl\(^1\) has attempted to estimate experimentally the therapeutical value of several balsams, especially of sandalwood oil and of preparations of sandalwood oil. It is familiar ground that the action of balsams is due to their power of arresting inflammation and exudation. With the object of ascertaining these inflammation-arresting properties in a measurable form, Pohl utilised a method devised by R. Winternitz. This consists in artificially provoking inflammatory symptoms in experimental animals of equal weight, and in applying the antidote under examination in one case. After a given period the matter exuded from the inflamed surfaces was then determined quantitatively, and the inflammation-arresting properties of the substance under examination were thus ascertained.

In each experiment Pohl injected into the pleura of three rabbits of approximately equal weight, heated yeast-suspension, an inflammatory agent. On the first and second day two of the animals were each given per os 2 cc. of the remedy under examination, mixed with alcohol and water. On the third day all three animals were bled to death, the thorax was opened and the exudations collected and measured in graduated test-tubes.

The results of the experiments, which are set forth in table-form, lead the author to pronounce sandalwood oil an active remedial agent. Its action is assisted by Kawa-

\(^1\) *Therap. Monatsh.* 26 (1912), 874.
Kawa, but biennial (santalyl carbonate) and allosane (santalol allophanate) are either insufficient or wholly inactive. The experiments with African copaiba balsam (*Balsamum africanum*) gave no definite result. Matico oil and gurjun balsam were ineffective. Santalol energetically arrests inflammation. Singularly enough the author describes santalol, which is in reality a sesquiterpene alcohol, as camphoric ester. Unfortunately it is impossible to determine whether Pohl in his experiments actually employed pure santalol, inasmuch as he fails to give any data concerning the physical and chemical properties of the preparations used by him. This also applies especially to the sandalwood oils employed in the experiments. Judging by the values given in his table the action of these oils was most unequal, which points either to great differences in their quality or to adulteration of some of the oils.

**Sandalwood Oil, West Indian.** The trade in West Indian sandalwood oil has profited from the advance in East Indian oil to this extent that sales have been brisker, because unfortunately West Indian oil plays a considerable part in the "cheapening" of the East Indian article. We have lately again made contracts for large parcels of West Indian wood, and we shall therefore doubtless be able to continue to supply our many customers in the future at advantageous prices.

**Sassafras Oil.** According to information received from our New York branch, there has lately been a more liberal supply of oil from the sources of production, and the difficulties to which we alluded in our last *Report* therefore appear to be removed. In making purchases our friends should act with the utmost caution, because adulteration with artificial sassafras oil, a camphor oil fraction manufactured in the United States, is very frequently resorted to. Cheap sassafras oils are always suspect, to say the least.

**Savin Oil.** It is becoming more and more difficult to procure savin oil of normal quality, because the collectors of the herb in the Tyrol are constantly demanding higher prices. Until such time as we are able to put an end to the inconvenience resulting from this state of things, great scarcity will continue to prevail in the article, and we have been compelled to increase our prices accordingly. It would be very desirable if new sources of production of the raw material (*Frondes sabinae*) were opened up, and we should be very grateful to our readers, especially to those who reside abroad, if they would interest themselves in this question.

**Shiu Oil.** According to a report by the British Consul at Tamsui on the trade of Formosa in the year 1911, the Camphor Monopoly Bureau has made attempts to prepare linalool on a large scale from shiu oil, concerning which matter we have repeatedly reported. The tree in question is probably a species of *Cinnamomum* or *Machilus*; it is known in Formosa as *Shā-shō-boku* or *Ch'ou chang* (= stinking camphor tree) while the oil is known as *Ch'ou yu* (= stinking oil).

The Monopoly Bureau is now in a position to supply about 65,000 lbs. shiu oil, but it is said that there is sufficient raw material available to raise the output to 250,000 or 300,000 lbs., the linalool-content of which is liable to great fluctuations.

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1) *Board of Trade Journal* 78 (1912), 650. Also comp. *Oil, Paint and Drug Reporter* 82 (1912), No. 15, p. 38; *Chemist and Druggist* 81 (1912), 454; *Perfum. and Essent Oil Record* 3 (1912), 239. — 2) Comp. our *Report* October 1912, 103.
The oil prepared by the Monopoly Bureau is said to contain about 60 p.c. linalool. The sale of the oil is in the hands of the Bureau, but so far nothing has yet been settled as to the countries to which it is to be exported or the price at which it is to be sold. The British Consul is of opinion that the crude oil can be prepared at half the price of linalool.

*The Perfumery and Essential Oil Record (loc. cit.*) describes two oils received from the Commercial Intelligence Branch of the Board of Trade in London, which fall under the above heading:

A (separated from a crude oil by repeated distillation). \( d_{150} 0,879, \alpha_D - 16^\circ \), ester (linalyl acetate) 6,4 p.c., total linalool 56,0 p.c.

B (separated by distillation from a crude oil of high sp. gr.). \( d_{150} 0,883, \alpha_D - 14^\circ \), ester 0,9 p.c., total linalool 47,1 p.c.

**Spearmint Oil.** The increase in the production, of which we have recently been advised by our New York friends, has had no weakening effect upon the market, but consumption has increased to such an extent that the available supplies of oil will most probably be insufficient to carry us over to the time of the arrival of the new crop. The bulk of the production is consumed in the United States. Within the past few months the prices have repeatedly become firmer, and we have at last been compelled to follow the market with our quotations.

**Spike Oil.** As already mentioned in our October *Report*, the French producing centres have been of no account so far as the supply of any considerable quantity is concerned, as the prices asked have been quite out of the question. As a result, all those interested in the oil turned their attention to the Spanish producing districts, where something like a struggle to secure supplies has set in, unfortunately with the unavoidable result that the prices were gradually being rushed upwards. We have been able to make very advantageous contracts and we are therefore in a position to offer oil of a quality which is identical with that previously received from France, at comparatively low prices. Of course for many technical purposes the present range of values of spike oil precludes its use, but in default of any cheap substitute (owing to its imperfect solubility and its peculiar odour, rosemary oil is usually out of the question for this purpose) we are afraid that, with good or ill grace, consumers will be compelled to pay our price. In order to make things as easy as possible for our friends we shall be satisfied with a very modest profit.

**Star Anise Oil.** The price of star anise oil (Red Ship Brand) has fluctuated as follows in the course of the winter:—

<table>
<thead>
<tr>
<th>Date</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st October</td>
<td>1912 6/-</td>
</tr>
<tr>
<td>15th</td>
<td>1912 6/-</td>
</tr>
<tr>
<td>1st November</td>
<td>1912 5/11s</td>
</tr>
<tr>
<td>15th</td>
<td>1912 5/11</td>
</tr>
<tr>
<td>1st December</td>
<td>1912 6/2</td>
</tr>
<tr>
<td>15th</td>
<td>1912 6/2</td>
</tr>
<tr>
<td>1st January</td>
<td>1913 6/4</td>
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<tr>
<td>15th</td>
<td>1913 6/2</td>
</tr>
<tr>
<td>1st February</td>
<td>1913 6/1</td>
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<tr>
<td>15th</td>
<td>1913 5/11</td>
</tr>
<tr>
<td>1st March</td>
<td>1913 5/10</td>
</tr>
<tr>
<td>15th</td>
<td>1913 6/3</td>
</tr>
</tbody>
</table>

The characteristic feature of the period under review has therefore been the continuous up-and-down movement of the quotations, and it would appear that this movement has been solely determined by the relation between supply and demand and
by fluctuations in the rate of exchange. There does not appear to have been any
dearth of oil, or else the uncertain state of the market would assuredly have given
way to a decided increase in prices. Last year's output of Tonquin oil is practically
sold out and new oil is not yet on offer.

**Taraxacum Root Oil.** From the alcoholic extract of taraxacum root (*Taraxacum
officinale*, Web., N. O. *Compositae*) F. B. Power and H. Browning¹ have obtained traces
of a volatile oil of a deep yellow colour, in which they detected furfurol by means
of the colour-reaction.

**Thyme Oil** has shown no variations in price. The market has been fairly quiet
and at times the sale left much to be desired, especially because this oil suffers very
seriously from the competition of cheap and inferior qualities.

C. Kleber² raises the objection to the method laid down in the U. S. Pharmacopœia
for the estimation of thymol in oil of thyme, that the prescribed quantity of liquor is
insufficient. Even when the phenol-content is only 20 p.c., he says, 20 cc. of 5 p.c.
soda-liquor are insufficient for 10 cc. oil, because owing to the fact that thymol and
carvacrol are only faintly acid, these constituents are in part retained by the non-
phenols unless a sufficient excess of alkali is present.

Kleber carries out the estimation with 4 p.c. soda liquor in a cassia-flask. He
first fills this with the liquor up to the 0-mark and then adds the oil under examination
up to the top-mark (either 6 or 10 cc. according to the graduation of the neck of the
flask). He then stops the flask with a cork, turns it over in order to allow the oil
to ascend into the bulb, and shakes for several minutes. After this he allows it to
stand, reads off, and converts into percentages.

We may here add that in a Supplement to the U. S. Pharmacopœia dated 1 June, 1907,
the quantity of 5 p.c. liquor to be used in the estimation of phenol in oil of thyme has
been increased from 20 to 40 cc., which, we should say, disposes of the subject.

**Tuberose Oil.** The tuberose plantations in the South of France are suffering much
from a disease which is locally known simply as *maladie des tubéreuses*, but of which
the origin was unknown there. From an article by F. R. Varaldi³ we observe that the
cause of the affection has now been traced to the same nematode which causes the ring-
disease of the hyacinth-bulbs and which is injurious to many other cultivated plants. In
order to destroy the pest, Varaldi recommends treating the soil with carbon disulphide.

**Turpentine Oil.** For a considerable time turpentine oil (either newly-distilled or
so-called "ozonised") has been used, together with hydrogen peroxide and perman-
ganate of potassium, as an antidote in poisoning with yellow phosphorus. A large
number of scientists have within recent decades carried out chemical and toxicological
investigations into this subject, but up to the present there has been so great a divergence
between their views on the efficacy of turpentine oil in phosphorus-poisoning that the
oil could not be said to be a universally recognised remedy. Some authors regard the
action of the oil as due to the formation of oxidation-products of phosphorus, whereas
others deny altogether that it has any effect upon phosphorus at all. According to

more recent investigators, such as Minovici\textsuperscript{1}) and Colson\textsuperscript{2)}, the action of the antidote in question is due to the formation of a peculiar non-toxic compound, so-called turpentine-phosphorous acid. For the reasons abovementioned E. Sieburg\textsuperscript{3}) has set himself the task of clearing up these contradictory views by an experimental chemical and toxicological investigation. With this object in view, Sieburg ascertained by analysis the conditions which govern the formation of the compound in question and its empirical formula, and, by experiments with living animals, tested its action and its behaviour in the animal organism. In view of the general interest which attaches to the whole problem we deem it desirable to refer in some detail to the results of this investigation.

According to Sieburg, so-called turpentine-phosphorous acid is prepared as follows: In a round flask on a boiling water-bath, from 2 to 5 p. c. (under circumstances also 10 p. c.) of yellow phosphorus is dissolved in freshly-distilled or oxidised French turpentine oil, by passing-in air. The solution is left standing for some time in open dishes. The oil turns turbid and soon afterwards the turpentine-phosphorous acid separates out in the shape of a film. When this is removed another film forms, until all the phosphorus is used up. From the fact that no film is formed when the reaction takes place in filled and closed vessels it is to be inferred that the formation is due to the action of atmospheric oxygen. When the filmy product is pressed it constitutes a sticky, wax-like body, which after treatment with light petroleum appears as a colourless, dry, powdery mass, incapable of being purified by crystallisation. At 82° the mass is melted and, when exposed to air, it resinsifies somewhat rapidly. According to Sieburg its odour is peculiar and does not clearly remind of phosphorus; it dissolves readily in alcohol, chloroform, and acetone, sparingly in light petroleum, ether and benzene. With litmus-paper the solutions give an acid reaction. When dissolved in alkalis, the body is precipitated again when hydrochloric acid is added. It exhibits marked reducing properties towards alkaline solution of silver or copper. The author assigns to the body the empirical formula \( \text{C}_{10}\text{H}_{15}\text{P} \text{O}_3 \) or \( \text{C}_{10}\text{H}_{15}\text{P} \text{O}_4 \text{HO} \). The analysis of the sodium-, barium-, and lead-salt shows the compound to be of the nature of an unibasic acid. It does not absorb bromine. Oxidation with nitric acid gives rise to phosphoric acid. When warmed to 100° the substance decomposes, giving off phosphoretted hydrogen (?). When heated above 180° a faintly-yellow liquid free from phosphorus passes over which, when brominated in carbon disulphide solution, yields crystals, m. p. 96. These, Sieburg regards as pinoldibromide \( \text{C}_{10}\text{H}_{15}\text{Br}_2\text{O} \). By means of alcoholic potash the solid body was converted into a liquid with a faint camphoraceous odour, b. p. 187°, which may be pinol \( \text{C}_{10}\text{H}_{16}\text{O} \). In view of the results stated above Sieburg (herein differing from Minovici, who has assigned to the compound the formula \( \text{C}_{10}\text{H}_{18}\text{H}_2\text{PO}_3 \)), believes that the body should be regarded, not as a derivative of phosphorous acid, but as one of hypophosphorous acid, possessing the structure

\[
\text{P} \quad \text{O} \quad \text{OH} \quad \text{P}\text{O} \quad \text{O} \quad \text{OH} \\
\text{C}_{10}\text{H}_{16}\text{O}
\]

Hence he gives it the name of "pinolhypophosphorous acid".

Pending the publication of the results of further investigations into the constitution of this body we feel unable to share the author's view. In the first place, the fact that pinol occurs when the decomposition takes place above 180° by no means proves that

\textsuperscript{1) Pharm. Zentrath. 45 (1904), 532. — 2) Compt. rend. 146 (1908), 817; Report November 1908, 124. — 3) Biochem. Zeitschr. 43 (1912), 280. From a reprint kindly sent to us. — 4) The empirical formula \( \text{C}_{10}\text{H}_{15}\text{P} \text{O}_3 \) is theoretically quite out of the question. In that case it would have to be \( \text{C}_{10}\text{H}_{18}\text{P} \text{O}_3 \).}
when phosphorus is allowed to act upon pinene under access of air, an absorption of oxygen by the pinene-molecule under formation of pinol actually does occur. Pinol may not be formed until decomposition has set in. Moreover, it is questionable whether the notation given above correctly represents the molecular structure, because the chaining of the pinol molecule with the radical of the acid by means of a double bond is not very probable, altogether apart from the fact that, if this did occur, the molecule would acquire the formula $\text{C}_{10}\text{H}_{14}\text{O}$. Perhaps a more correct formula would be: $\text{O} = \text{P}^+\text{H}^{-}$. Eventually the formula of a molecular modification $\text{C}_{10}\text{H}_{19}\text{PO}_{3}$ or $\text{C}_{10}\text{H}_{15}\text{O}$, $\text{H}_{3}\text{PO}_{4}$ must be taken into account, as the analytical values ascertained by Sieburg may also apply to this.

In experiments in the synthesis of turpentine-phosphorous acid the author heated both newly-distilled and oxidised pinene with phosphorous- and with hypophosphorous acid in a reflux condenser, as well as with phosphorus trichloride, adding aluminium chloride, but with negative results. Nor did the desired reaction occur when hydration-products of pinene, such as terpineol and terpin hydrate were heated with phosphorus. Sieburg has not carried out these reactions with pinol.

Experiments with chickens, rabbits, and dogs showed not only that pinol hypophosphorous acid has ceased to have any effect of phosphorus, but also that it is completely non-toxic. It is eliminated in the urine of the experimental animal in the form of pinol phosphorous acid. No formation of combined or free glucuronic acid in the animal organism was observed. The antibacterial properties of the body are negligible.

In conclusion we reproduce verbatim Sieburg's summary of the results of his investigations.

1. From turpentine oil (pinene) and phosphorus a compound is formed extra corpus. This body should not be designated as turpentine-phosphorous acid.
2. Terpenol-hypophosphorous acid is a better name for it.
3. Those salts of the body which have been analysed, viz., the Na-, Li-, Ba-, and Pb-salt, indicate an unibasic acid.
4. When gently oxidised in a test-tube it gives rise to terpenol-phosphorous acid.
5. The non-toxic terpenol-hypophosphorous acid undergoes a similar, albeit not identical, conversion in the animal organism, as it does when gently oxidised in a test-tube, that is to say, it is eliminated in the form of terpenol-phosphorous acid $\text{P(OH)}_{3}\text{OC}_{10}\text{H}_{17}\text{O}$.
6. This behaviour at the same time supports the assertion that the product of reaction of phosphorus upon terpene is a chemical compound of this character; also, that in the said substance the phosphorus is intimately attached to the hydrocarbon, as otherwise according to all experience the last-named would be eliminated from the organism in the form of a glucurone-combination.

The question, extremely important from a medical point of view, whether the formation of a non-toxic body as a result of the action of terpenes upon phosphorus in the presence of oxygen is capable of being practically utilised in cases of phosphorus-poisoning, is to be treated by the author in a subsequent paper.

In connection with the above we desire to make known the experiments in the preparation and purification of so-called turpentine-phosphorous acid, which were carried out by us as long ago as the years 1903 and 1904. The experiments were not con-
continued long at the time for the reason that, especially with oxidised turpentine oil, they repeatedly resulted in explosions.

In 60 grams French turpentine oil (d_{150} 0.9890; \(a_\beta - 29^\circ 46'\)) which had been oxidised for 50 days by passing-in air, we dissolved 1.5 grams of white phosphorus by heating on the water-bath, after which the closed vessel was left standing for some time in a cool place. During this time traces of luminous crystals were deposited, which began to resinify as soon as the substance was filtered off. On subsequent cooling no further crystallisation and no formation of a film took place.

When the above experiment was repeated with 80 grams oil and 2 grams white phosphorus in a round flask with a rising tube, the entire mass exploded after being vigorously shaken.

In 100 grams of the fractions of French turpentine oil which boil between 160 and 163\(^\circ\) (d_{150} 0.8683; \(a_\beta - 31^\circ 15'\)) we dissolved 3 grams white phosphorus at 60\(^\circ\) in a water-bath. Overnight a somewhat soft, colourless mass had separated out in the form of a film on the surface of the liquid. When treated with light petroleum this mass became tolerably dry, but when left exposed to the air it soon commenced to resinify again and finally it became entirely liquid. The wax-like mass, when placed on porous tiles, had an odour somewhat like garlic and an inconstant m.p. of from 82 to 85\(^\circ\). It keeps fairly well for some time in tubes filled with carbon dioxide. When left standing a solid body again separated out from the filtered liquid. This body was incapable of recrystallisation. It is sparingly soluble in water, ether, and light petroleum, but dissolves readily in acetone and chloroform. When dissolved in soda-liquor it again separates out on addition of hydrochloric acid. We did not analyse the substance.

Vèzes and M\(^{me}\) Pariselle\(^1\) divide the numerous substitutes of turpentine oil into two classes. The first contains the substitutes which are allied to so-called "white spirit"; to the second belong those products which are obtained from tarry wood by dry distillation, extraction, distillation with superheated steam, or by any other method. The authors give detailed physical data, which we are unable to reproduce here.

By the aid of a thermoturpentinometer constructed by Tortelli\(^2\), R. Massy\(^3\) has made careful experiments in the detection of petroleum in French turpentine oil\(^4\) (from \textit{Pinus Pinaster}, Sol.). The method is based upon measuring the rise in temperature which ensues when sulphuric acid (d_{150} 1.722) is added to the sample of turpentine oil under examination, under stirring. This difference in temperature is called "thermoturpentine degree", and according to Tortelli it should amount to from 100 to 105\(^\circ\) in the case of turpentine oils of good quality, using 10 cc. each of sulphuric acid and turpentine oil. Contrary to Tortelli's practice, Massy does not make the test with the crude oil, but with a fraction of the oil. From 25 cc. he distils off 20 cc. in which he carries out the test. Massy found the thermoturpentine degrees of 15 samples of French turpentine oil of good quality to range from 96.2 to 100.6\(^\circ\). The addition of burning oil (lamp oil), rectified mineral oil, white spirit, carbon tetrachloride, and benzene reduce the thermoturpentine degree, whereas if colophony or heavy mineral

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oil is present the degree is not affected, because those substances remain behind in the residue.

Tortelli's method bears some relation to the familiar sulphuric acid test\(^1\) of Maumé, which is used in the examination of fatty oils. The reaction was applied to essential oils by R. Williams\(^2\) over 20 years ago, but it did not prove reliable and was consequently abandoned for this purpose. After this experience we regard it as very doubtful whether, either in the form recommended by Tortelli or by Massy, this method will acquire a lasting place among the processes for testing oil of turpentine.

Massy has treated the subject in greater detail in a pamphlet bearing the title "A la recherche d'un procédé simple d'essai de l'essence de térébentine" (Bordeaux 1913)\(^3\). In this publication the author also deals exhaustively with a method for the detection of adulterations which has already been recommended by him on a previous occasion, and in which he tests the behaviour of the oil, distilled by the method mentioned above, towards 80,7 p.c. alcohol. We have already mentioned this matter in our Report of April 1911 (p. 115).

The differentiation of turpentine oil from camphor oil is referred to on p. 38.

On the detection of petroleum in turpentine oil see p. 129.

It may be stated that H. Wolff\(^4\) has found the mean coefficient of distension of turpentine oil to be 0,00100 per 10\(^o\). The correction required in determining the refrac- tion is 0,00037 per 10\(^o\). Coste\(^5\) had already given the same correction.

An American trade journal\(^6\) discusses a Report of the Forestry Division of the Department of Agriculture which deals with the possibility of obtaining turpentine oil and other naval stores from the trees which in the United States are known as the Western Pines. The labour-question plays an important part in the matter, seeing that in Arizona and California the people are quite ignorant of the methods of tapping, and that it would be too expensive to bring labour from the South-Eastern States. Moreover, the severe winters of the Western States are unfavourable for the production of turpentine. But until experiments have been made on a large scale, it is impossible to form a judgment of the prospects of the production of turpentine there.

In connection with the above report we may here refer to an article by A. W. Schorger\(^7\) in which he enumerates the characters and the constitution of the turpentine and turpentine oils of some of the Western pines. From the turpentine of *Pinus ponderosa*, Laws. (Western Yellow Pine) the author obtained 18,5 p.c. of a volatile oil possessing the following constants: \(d_{150} 0,8625, [\alpha]_D - 14,39^\circ, n_{D20} 1,4772\). He found the oil to contain the following constituents: about 5 p.c. \(\alpha\)-pinene (nitro- piperidine, m. p. 118\(^o\)), 60 to 70 p.c. \(\beta\)-pinene (n opinic acid, m. p. 126\(^o\)), and 20 to 25 p.c. \(\beta\)-limonene (tetrabromide, m. p. 104\(^o\)). *Pinus ponderosa scopulorum*. Engelm., a degenerate species of the last-named which occurs in the Rocky Mountains, yields a turpentine containing 19,6 p.c. oil with the following constants: \(d_{150} 0,8639\) to 0,8672, \([\alpha]_D + 12,86\) and + 13,03\(^o\), \(n_{D20} 1,4727\). It contained 60 to 70 p.c. of \(\alpha\)-pinene (nitrosochloride, m. p. 103\(^o\)), 5 p.c. \(\beta\)-pinene (n opinic acid, m. p. 125\(^o\)) and 20 to 25 p.c. limonene.

(tetrabromide m. p. 104.5°). In agreement with the statements made by previous authors¹), Schorger found the turpentine oil of the "Digger Pine" (Pinus Sabiniiana, Dougl.) to contain only n-heptane. From the turpentine he recovered 11.4 p. c. of oil possessing the following characters: b. p. 96.1 to 98.8°, d₁₅₀ 0.6971, nD₁₅₀ 1.3903. The turpentine of the "Sugar Pine" (Pinus Lambertiana, Dougl.) yields 16.3 p. c. turpentine oil with a density of 0.8658 to 0.8663 at 15°; [c]₀ + 10.42°; nD₀ 1.4728. This oil contains 70 to 75 p. c. d-α-pinene (nitrosochloride, m. p. 103°), 5 p. c. β-pinene (nopicinic acid, m. p. 125°) 2 to 3 p. c. of a terpene mixture in which perhaps phellandrene occurs, 2 to 3 p. c. of an aliphatic hydrocarbon and 10 to 12 p. c. of a sesquiterpene of which the properties agree fairly well with those of the aromadendrene of the Australian eucalyptus oils described by Baker and Smith ²): b. p. 250 to 255° (739.9 mm.), d 0.9238, [α]₀ + 37.88°, n₀ 1,5006. The turpentine of Pinus contorta (= murrayana), Loud. (Lodge Pole Pine), when distilled with steam, yielded 14.7 p. c. oil (d₁₅₀ 0.8518 to 0.8549; [α]₀ − 20.12°; nD₁₅₀ 1.4862) consisting almost entirely of l-β-phellandrene. Schorger identified the terpene by preparing its nitrite; m. p. 90° under slow, 103° under rapid heating. Up to the present phellandrene had not yet been observed among the constituents of turpentine oil. Of the turpentine oil of Pinus edulis, Engelm. (Piñon Pine) 20 p. c. was obtained: d₁₅₀ 0.8680, [α]₀ + 19.26°, nD₁₅₀ 1.4707. It consisted to the extent of from 70 to 75 p. c. of α-pinene (nitrosochloride, m. p. 103°) and also contained 5 p. c. β-pinene (nopinic acid, m. p. 123°) and from 15 to 20 p. c. d-cadinene which was identified from the dihydrochloride, m. p. 118°. Cadinene, too, was not yet known as a constituent of any turpentine oil.

A. Hasterlik ³), in an article written in an animated style and beautifully illustrated, describes the preparation of the "Balsams of Gascony" as he calls the turpentine made in that district. He mentions the French engineer Chambrelent as the man who was the maker of this erstwhile desolate region. About the middle of the 19th century, in the course of his numerous journeys on official service, Chambrelent had become well acquainted with the "Landes" country, and had observed that interspersed by small patches of pine-trees (pignades) were vast empty stretches of country without a blade of grass. The fact that the soil where the pine-trees flourished did not differ in its composition from the desolate places led him to the assumption that the difference in vegetation was due to different conditions of drainage. If it were possible to equalise the supply of moisture over the entire district, he thought, it ought to be an easy matter to enlarge the as yet meagre pine-growth into a considerable forest-area. As a result of his hydrographic investigations Chambrelent found that the highest point of the Landes formed a plain at an elevation of 107 meters above sea-level, gradually sloping away towards the ocean at a gradient of 1:1000. Underneath a sandy stratum varying in depth from 35 to 60 centimetres was a stratum impermeable by water and below that, at a depth of 8 to 10 meters, another layer of sand conducting water⁴). Therefore, the digging of a ditch of a little over half a meter in depth, and with exactly the same gradient as the slope of the land, should suffice to overcome the waterlogging and to ensure a slow but steady water-drainage. Chambrelent appealed to the Government, giving a careful resumé of his findings, but he was unsuccessful. It was not until he was able to shew excellent results with the plantations he had made on his own property, and had laid the first achievements thereof before the jury

at the Paris Exhibition of 1855, that the Government accepted his suggestions, and on June 19, 1857 legal measures were enacted for reclaiming the Landes according to Chambrelent's plans.

Hasterlik does not mention the experiments in cultivation made by Brémontier, although it is true that these were restricted to the sandy dunes bordering the sea. Brémontier, in the years 1787 to 1793, systematically carried out his plan for counteracting the movement of the soil of these sandhills, and his system is still carried out by the Government. The forests on the dunes extend over about 20,000 acres, but they only constitute about one-tenth of the entire forest area of South Western France of which the existence is due the suggestions made by Chambrelent.

Detailed particulars of the turpentine oil industry in the Landes are given in a lengthy article by Vèzes. He accurately describes and figures the modern stills, and enumerates the many patents in a separate schedule.

At present the turpentine oil which is prepared in British India is consumed within the country itself; but there is a possibility that larger quantities may be distilled in the future and that the oil may make its appearance upon the European market. For this reason the Imperial Institute, London, has examined a series of samples of turpentine oil from Pinus longifolia and determined their constants as well as their behaviour on boiling. In comparison with the ordinary turpentine oil of commerce it is noteworthy that the oil from Pinus longifolia contains very few constituents of low boiling point, a fact to which we have already called attention. The Imperial Institute has also discovered that Indian turpentine oil evaporates more slowly, and leaves a larger residue of resin, than does the turpentine oil of commerce. It is true that zinc resinate is more readily soluble in ordinary than in Indian turpentine oil, but it would appear that in spite of this the latter product may be used in the preparation of certain varnishes.

With regard to its commercial value, Indian turpentine oil probably equals the exported Russian turpentine oil (see p. 104).

The table below shows the behaviour on boiling of a crude and of a rectified turpentine oil from Pinus longifolia and of an ordinary turpentine oil bought in London:

<table>
<thead>
<tr>
<th>B. P. of Fraction</th>
<th>From Pinus longifolia</th>
<th>From ordinary turpentine oil bought in London</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crude Oil</td>
<td>Rect. Oil</td>
</tr>
<tr>
<td>up to 165°</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>165° — 170°</td>
<td>43 p.c.</td>
<td>56 p.c.</td>
</tr>
<tr>
<td>170° — 175°</td>
<td>40 p.c.</td>
<td>33 p.c.</td>
</tr>
<tr>
<td>175° — 180°</td>
<td>8 p.c.</td>
<td>4,5 p.c.</td>
</tr>
<tr>
<td>180° — 190°</td>
<td>3 p.c.</td>
<td>1,5 p.c.</td>
</tr>
<tr>
<td>190° — 195°</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Residue and loss</td>
<td>6 p.c.</td>
<td>5 p.c.</td>
</tr>
</tbody>
</table>

Samples of turpentine oil from Pinus excelsa and P. Khasya, which had been sent to the Institute from Dehra Dun were also examined.

The constants of the turpentine oil from Pinus excelsa were as follow: \( d_{40}^{10} 0,862, a_p + 36^\circ 40' \). 74 p.c. of the oil boiled between 157 and 158° \((a_p + 37^\circ 10')\), 16 p.c.

between 158 and 160° (α<sub>D</sub> + 36° 15′), 7 p. c. between 160 and 170° (α<sub>D</sub> + 34° 10′), residue 3 p. c. The crude product is yellow, the rectified oil is colourless. As the principal portion of the oil consists of d-pinene, it must be regarded as a turpentine oil of good quality.

The turpentine oil from <i>Pinus Khasya</i> contained fewer low-boiling constituents and may be compared with American turpentine oil of low quality: d<sub>20</sub> 0,870, α<sub>D</sub> — 4° 50′, behaviour on boiling: 162 to 163° 25 p. c. (α<sub>D</sub> — 1° 50′), 163 to 165° 57 p. c. (α<sub>D</sub> — 4° 40′), 165 to 169° 11 p. c. (α<sub>D</sub> — 10° 40′), residue and loss 7 p. c. (α<sub>D</sub> — 7° 30′). It is evident from the rotation of the separate fractions that the oil is composed of various terpenes. The crude product was of a yellow colour; after rectification it was colourless.

Vèzes<sup>1)</sup> mentions as a new source of raw material for the preparation of pinene the familiar turpentine oil of the Aleppo pine and that of <i>Pinus Massoniana</i>. He examined eleven samples of Aleppo pine oils (from <i>Pinus halepensis</i>, Mill.) and found their average constants to be as follow: d<sub>25</sub> 0,8546 to 0,8568, [α]<sub>D</sub> + 46,5 to + 47,8°, n<sub>D25</sub> 1,4638 to 1,4652.

<i>Pinus Massoniana</i>, Sieb. et Zucc. (<i>P. Thunbergii</i>, Parl. of the Index Kewensis), a tree which grows on the high plains of British India and Burma, affords about 21 p. c. of turpentine oil: d<sub>25</sub> 0,8532 to 0,8511, [α]<sub>D</sub> + 31,6 to 42° 4′, n<sub>D25</sub> 1,4645 to 1,4650. This oil, like that mentioned above, consists almost entirely of d-pinene.

We may here also refer to a turpentine oil from <i>Pinus cambodgiana</i><sup>2)</sup> which has been obtained by A. Wichmann<sup>3)</sup> from the resin (place of origin, French India) by steam distillation. The yield was 19,35 p. c. The oil constitutes a pale yellow liquid with a pleasant aromatic, turpentine-like odour. d 0,892; n<sub>D20</sub> 1,48455.

Some time ago we mentioned a British Consular Report from Hakodate<sup>4)</sup> according to which the preliminary attempts at manufacturing turpentine oil in the Japanese section of the Island of Sakhalien had been very successful. An official Japanese publication<sup>5)</sup> contains the following note on the forest-wealth of Sakhalien:

The forests are of a virgin character and of an extent unapproached by any other in the Japanese Empire. They may be described as inexhaustible. Among the conifers the principal are the Todo pine (<i>Abies sachalinensis</i>) the Yeso pine (<i>Picea ajanensis</i>) and the larch. Owing to its high resisting power the latter is particularly adapted for telegraph-posts, railway-sleepers, and bridge-material. The forests are also capable of producing turpentine oil and colophony from the larch-turpentine, wood spirits, tar, pitch and many other materials; and there is no doubt that before long a chemical industry for the by-products of forestry will develop. As the forests occur mostly on the high plateaux or in valleys with a gentle slope, the snow in winter affords an easy means for the transport of the felled trees and renders the forests more accessible. When shortly the exploitation of the forests is taken in hand, the forest-wealth, together with fisheries and mining, will prove a rich source of revenue.

Schindelmeiser has written to E. J. Parry<sup>6)</sup> to inform him that normal Russian turpentine oil is never shipped to England at all. The fractions with the boiling point of American turpentine oil are removed from the oil in Russia and are used in that country itself for industrial purposes, while the mixture of the high- and the low-boiling

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<sup>1)</sup> 8th International congress of applied chemistry, Vol. 12, p. 211. From a reprint kindly sent to us.
<sup>2)</sup> The author is not mentioned.
<sup>3)</sup> Arch. der Pharm. 250 (1912), 472. — <sup>4)</sup> Report April 1911, 117. —
<sup>5)</sup> Finanz. u. wirtsch. Jahrbuch f. Japan 12 (1912), 204. — <sup>6)</sup> Chemist and Druggist 81 (1912), 655.
fractions is exported under the name of "Russian turpentine oil." According to Schindelmeiser the original product contains from 40 to 70 p. c. of fractions boiling between 155 to 160°, consisting chiefly of pinene.

Parry mentions the following constants as being characteristic of genuine rectified Russian turpentine oil: d 0.8646, $$\alpha_d + 8^\circ$$, n 1,4890. From 68 p. c. of the oil boils between 155 and 160°.

L. F. Hawley and R. C. Palmer¹) have gone thoroughly into the preparation of so-called wood-turpentine. They have come to the conclusion that it is difficult to set up general rules to be observed during the distilling process. For instance, it is impossible to recommend a definite degree of steam-pressure, for not only the oil-yields, but also the cost of getting up steam under pressure must be taken into consideration. In breaking up the wood, not only the desired oil-yield, but also the utilisation of the exhausted chips must be taken into account.

The authors made the interesting discovery that dipentene is pre-existent in the wood itself, and is not formed only during the distilling. Exhausted sawdust was mixed with 1,175 p. c. turpentine and steam-distilled both at ordinary and at raised pressure. The essential oil thus obtained contains no dipentene, but in wood-turpentine the presence of this terpene may be detected by its tetrabromide, m. p. 125 to 126°.

Leuchter²) recommends for the differentiation of turpentine oil and pine tar oil reactions with phloroglucinol or nitrobenzaldehyde. Turpentine oil assumes a palish yellow colour in a solution of phloroglucinol with a mixture of dilute alcohol, glycerol and hydrochloric acid, while pine tar oil turns pink to ruby red. With a solution of o-nitrobenzaldehyde in aqueous-alcoholic soda liquor (about 2 p. c.) turpentine oil acquires a bright yellow colour, while pine tar oil turns yellowish-brown to black. These reactions are said also to make it possible, up to a certain degree, to ascertain whether pine tar oil or so-called cellulose oil has been added to oil of turpentine, inasmuch as with cellulose oil the reaction is either weak or is entirely absent. The nitrobenzaldehyde reaction rarely fails with pine-tar oils.

Valerian Oil. The anatomy of the oil-cells of valerian root is referred to on p. 132.

Vetiver Oil. We are so excellently placed for procuring vetiver root of the finest quality from all the different countries of production, that we are able to take the utmost advantage of our direct supplies. The quality of our stocks of oil is exceptionally fine, and we must not omit to call attention to the fact that our price has lately been reduced again. The quotations for pure Réunion-oil are out of proportion high, although the official export statistics appear to indicate that there is by no means any scarcity of supplies, the exports in 1912 having reached 1421 kilos, as compared with 975 kilos in the previous year. In 1910 the shipments amounted to 1007 kilos. It would therefore appear that the upward movement is due to speculative manipulations, but to these we have grown accustomed with Réunion products.

Several years ago Genvresse and Langlois³) ascertained the presence in vetiver oil of a hydrocarbon, vetivene, C₁₉H₃₄, an alcohol, vetivenol, C₁₅H₉₉O, and an ester

derived from the said alcohol and the acid C_{15}H_{24}O_2. According to the most recent investigations, which have been conducted by F. W. Semmler, F. Risse, and F. Schröter\textsuperscript{1)}, the formulæ given by Genvresse and Langlois are incorrect, the proper notations being, for vetivenol C_{15}H_{24}O and for the acid C_{15}H_{22}O_2. The last-named investigators examined an oil distilled by us, and possessing the following properties: d_{200} 1,0239, \( \alpha_d + 31^\circ \), \( n_d \) 1,52552. They first resolved 400 grams of this oil, at 12 mm., into the following four fractions:—

A) B. p. 129 to 175°, 23 p. c.

B) B. p. 170 to 190°, 34 " "

C) B. p. 190 to 250°, 8 " "

D) B. p. 250 to 300°, 30 " "

Fraction D, when subjected to further distillation, was split up into two portions, as follows:—

D, a) B. p. 138 to 260° (13 mm.), 28 p. c.

D, b) B. p. 260 to 298° (13 mm.), 62 " "

Analysis showed beyond doubt that the portion D, b consisted of an ester C_{30}H_{44}O_2 of the acid C_{15}H_{22}O_2 and the alcohol C_{15}H_{24}O. The characters of the free alcohol are as follow: b. p. 170 to 174° (13 mm.), d_{200} 1,0209, \( \alpha_d + 34^\circ 30' \), \( n_d \) 1,52437, mol. refr. found 65,94, calc. for C_{15}H_{22}O_2 = 66,00. Hence the vetivenol of this fraction can only be a tricyclic, simply unsaturated alcohol. The acid C_{15}H_{22}O_2 boils at 202 to 205° (13 mm.), is tricyclic, and is called vetivenic acid by the authors. Its methylester boils between 170 and 173° (18 mm.): d_{200} 1,0372, \( \alpha_d + 42^\circ 12' \), \( n_d \) 1,50573, mol. refr. found 71,05, calc. for C_{16}H_{24}O_2 = 71,31.

Fractions A and B, when subjected to repeated fractional distillation in vacuo yielded a fraction boiling between 173 and 180° (13 mm.), from which vetivenol was obtainable by treatment with phthalic anhydride. It therefore appears to be a primary alcohol. Tricyclic vetivenol is capable of being reduced to tricyclic dihydrovetivenol, C_{15}H_{26}O by means of hydrogen in the presence of platinum: b. p. 176 to 179° (17 mm.), d_{200} 1,0055, \( \alpha_d + 31^\circ \), \( n_d \) 1,51354. Vetivenol (tricyclic) yields an acetate, b. p. 180 to 184° (19 mm.); d_{200} 1,0218; \( \alpha_d + 28^\circ 48' \); \( n_d \) 1,50433; mol. refr. found 75,91, calc. for C_{17}H_{38}O_2 = 75,61. Fraction C, upon saponification, yielded an oil from which, under repeated distillation, there was obtained a portion boiling between 178 and 185° (19 mm.): d_{200} 1,0137, \( \alpha_d + 52^\circ 12' \), \( n_d \) 1,52822, mol. refr. found 66,81, calc. for C_{16}H_{24}O_2 = 66,00, calc. for C_{15}H_{24}O_2 = 67,71. This body, therefore, represents a mixture of bi- and tricyclic vetivenol. The acid of fraction C was identical with vetivenic acid. The fractions A and B also contained a primary bicyclic vetivenol, which may possibly be identical with that from fraction C. These portions likewise contained tricyclic vetivenol.

Repeated fractionation in vacuo of fraction A, the ultimate fractionation being conducted over sodium, yielded two hydrocarbons:

I. B. p. 123 to 130° (16 mm.); d_{200} 0,9355; \( \alpha_d + 2^\circ 16' \); \( n_d \) 1,51126; mol. refr. found 65,32; calc. for C_{15}H_{24}/2 = 64,45, calc. for C_{15}H_{24}/2 = 66,15.

II. B. p. 137 to 140° (16 mm.); d_{200} 0,9321; \( \alpha_d - 10^\circ 12' \); \( n_d \) 1,51896; mol. refr. found 66,42 calc. for C_{15}H_{24}/2 = 64,45, calc. for C_{15}H_{24}/2 = 66,15.

According to the molecular refractions, fraction I should consist substantially of a tricyclic simply unsaturated hydrocarbon, while fraction II was to be regarded as

\textsuperscript{1) Bozl. Berichte 45 (1912), 2347.
the bicyclic doubly unsaturated hydrocarbon. They probably belong to the vetivenols C_{15}H_{24}O, just as the santalenes belong to the santalols, and should be differentiated as bi- and tricyclic vetivene.

The examination of Réunion vetiver oil (d_{20} 0.9916 and 0.9982; \( \alpha_d^\circ + 24^\circ 6' \) and +310; n_p 1,52429 and 1,52517) gave somewhat different results. The high-boiling constituent vetivenolic vetivenate, is either absent from this compound, or only occurs in it in scarcely detectable traces. The Réunion oil, like that distilled by us, contains tricyclic and bicyclic vetivene. The tricyclic as well as the bicyclic vetivenol also occur in the Réunion oil.

In the course of reaction with phosphorus pentachloride in light petroleum solution, the vetivene from Réunion oil (b. p. 161 to 164\(^\circ\) at 9 mm.) formed a chloride with b. p. 140 to 147\(^\circ\) (10 mm.): d_{20} 0.9679, \( \alpha_d^\circ -24^\circ \), n_p 1,52640, from which latter a synthetic vetivene was obtained by reduction with sodium and alcohol: b. p. 121 to 127\(^\circ\) (9 mm.), d_{20} 0.9296, \( \alpha_d^\circ -25^\circ 48' \), n_p 1,51491, mol. refr. found 66.1, calc. for C_{15}H_{24}/\begin{array}{c} 5 \end{array} 66.07.

Semmler obtained a different result when, without previous distillation in vacuo, he reduced the chloride (which had also been prepared by means of phosphorus pentachloride), with sodium and alcohol. The resulting hydrocarbon was first distilled over sodium and then subjected to a prolonged shaking with a 3 p. c. permanganate solution; after which it possessed the following characteristics: b. p. 123 to 129\(^\circ\) (10 mm.), d_{20} 0.9288, \( \alpha_d^\circ +6^\circ 1' \), n_p 1,50682, mol. refr. found 63.88, calc. for C_{15}H_{24}/\begin{array}{c} 4 \end{array} 64.43.

Further investigation is needed to clear up the point in how far the synthetic and the natural vetivenes are identical.

Reduction of the crude vetivenol from Réunion oil by means of hydrogen in the presence of finely divided platinum led apparently to tricyclic dihydrovetivenol and bicyclic tetrahydrovetivenol. A small portion of the vetivenol was reduced to a hydrocarbon in the process.

**Oil of Wallflower seed.** It will be remembered that wallflower seed contains the isosulphocyanate cheirolines in glucoside-like combination, and that W. Schneider\(^1\)) has identified this body as a \( \gamma \)-thiocarbimidopropylmethylsulphone. Schneider, in collaboration with Lohmann\(^2\)), has recently reported on the glucoside, which is obtainable from the seeds (after removal of their fatty constituents) by extraction with anhydrous alcohol. The glucoside occurs as a substance without definite melting-point, and exceptionally readily soluble in water. When separated out from its alcoholic solution it still contains from 6 to 7 p. c. alcohol of crystallisation (\( ? \)) which, however, it gives off in vacuo over sodium at water-bath temperature. It was unfortunately impossible to prepare the glucoside in the pure state, its conditions of solubility being exceedingly unmanageable. Chemically it shows close analogy to other glucosides of mustard oil, and among its constituents are cheirolin, glucose, sulphuric acid, and potassium. Sulphur occurs in the glucoside-molecule in three modifications: as sulphuric acid, as allyl sulphide and as sulphonic sulphide. Cheirolin may be isolated by enzymatic decomposition with the myrosine of white mustard. The wallflower seed itself contains an enzyme which has the power of decomposing the sinigrine of black mustard (mustard oil being formed during the reaction), and which is therefore equal in value to, if not identical with, myrosine.

In searching for the presence of other sulphone mustard oils in the N. O. of the *Cruciferae*, the authors succeeded in proving the presence of allyl isosulphocyanate and

\(^1\) Liebigs Annalen 375 (1910), 207; Report October 1910, 85. — \(^2\) Berl. Berichte 45 (1912), 2954.
of myrosine in cauliflower-seed. The addition of ground cauliflower seed liberates allyl isosulphocyanate from the meal of black mustard in which the myrosine had previously been destroyed. The action of this allyl enzyme however, is very faint.

**Wintergreen Oil, American.** The market in the ordinary commercial product prepared from *Betula lenta* is entirely unchanged, business being regular, and from New York we hear that there is no alteration in prospect. Oil from *Gaultheria procumbens*, of which we keep no stock here, has also been distilled in sufficient quantities. The present price of the last-named variety is $4.50, or say 18 s. 9 d. per lb., a fact to which we only refer as a matter of curiosity.

According to H. D. Gibbs, R. R. Williams and D. S. Pratt¹) the yellow colour acquired by methyl salicylate when exposed to sunlight is due to a form of oxidation. It is not impossible that the yellow substance consists in the main of the methyl ester of *p*-quinone carboxylic acid. The yellow colour also develops in the dark in the presence of oxidising agents such as ozone, hydrogen peroxide, chromic acid, &c.

**Wormseed Oil, American.** After the arrival in Europe of the cheaper oil of last year’s crop, the prices could gradually be reduced. This reduction came very opportunely, especially because orders of considerable importance had been placed by pharmaceutical manufacturers. The efficacy of this anthelmintic is so generally admitted that we feel justified in forecasting a favourable future for American wormseed oil.

E. K. Nelson²) has continued his investigations into ascaridole, the principal constituent of American wormseed oil³). He stirred the oily conversion-product which is formed when ascaridole is heated to about 150°C, for 2 hours with 0.2 p.c. sulphuric acid, the oil being almost completely dissolved by this manipulation. By shaking the reaction-mass with ether, Nelson isolated from it the glycol, m. p. 62.5 to 64°C, which has already been described previously. He next shook out the exactly neutralised reaction-liquid with chloroform, thereby isolating a body with m. p. 62,5 to 64°C, which readily crystallises with one molecule of water. This compound Nelson calls *β*-glycol in order to distinguish it from the *α*-glycol, m. p. 62,5 to 64°C, which is referred to above. When heated with dilute sulphuric acid it yields thymol (m. p. of the phenylurethane 103 to 104°C). The neutral reaction-mass, after having been shaken out with chloroform, was evaporated and the residue extracted with anhydrous alcohol. By this method, Nelson obtained an erythritol C₁₀H₁₅O₄ which, when recrystallised from chloroform, had m. p. 128 to 130°C and which crystallises readily with one molecule of water. When boiled with dilute sulphuric acid it yields a ketone with an odour of menthone (semicarbazone m. p. 182 to 184°C) and a phenol-like body with m. p. 80 to 81°C. Nelson explains the formation of the erythritol (accepting Wallach’s ascaridole-formula⁴) as follows: Ascaridole (I), during heating is transposed into the body shown in formula II, from which latter it is converted by hydration into the erythritol m. p. 80 to 81°C, probably 1,2,3,4-tetrahydroxyterpane (III). If the erythritol really possesses this structure it must be capable of being oxidised into

$\alpha,\alpha'$-methylisopropyl-$\alpha,\alpha'$-dihydroxyadipic acid. As a matter of fact, when oxidised with permanganate of potassium in alkaline solution it yielded an acid melting at 190 to 191° which, when heated to 210° was converted into its anhydride and, when further heated to 250°, afforded the anhydride of ascaridolic acid. It is to be expected that the four possible optically active modifications of $\alpha,\alpha'$-methylisopropyl-$\alpha,\alpha'$-dihydroxyadipic acid are capable of forming two dilactones and two acid anhydrides. The fact that the acid with m. p. 190 to 191° is a substituted adipic acid, is evident from its behaviour under oxidation with potassium permanganate in acid solution. When subjected to this reaction it forms a ketone of which the semicarbazone melts between 201 and 202° and gives the pyrrol reaction when heated in a test-tube. The behaviour of the semicarbazone agrees with that of the semicarbazone of 2-methylheptane-3,6-dione, the oxidation-product of $\alpha,\alpha'$-methylisopropyl-$\alpha,\alpha'$-dihydroxyadipic acid.

By means of permanganate of potassium in acid solution Nelson has resolved the acid C$_{10}$H$_{16}$O$_3$, the oxidation-product of $\alpha$-glycol from ascaridole, into 2-methylheptane-3,6-dione (semicarbazone, m. p. 201 to 202°; oxime, m. p. 130 to 131°). Energetic oxidation of $\alpha$-glycol also affords 2-methylheptane-3,6-dione.

In order to explain the rise of the $\alpha$-glycol from ascaridole, Nelson assumes the transposition-product (II) to be a labile dioxide which is converted into $\alpha$-glycol (V) by way of the stable modification (IV). In that case the acid obtained from $\alpha$-glycol must be 1,4-cineolic acid (VI).

By reacting with saturated oxalic acid solution upon the anhydride of $\alpha$-glycol there was obtained the same phenol-like body which had resulted from $\alpha$- and $\beta$-glycol by heating with dilute sulphuric acid. It is an isomeride of diosphenol, but it does not reduce either Fehling's solution or ammoniacal silver-solution. When the $\alpha$-glycol anhydride is heated with benzoic acid it yields, in lieu of the expected benzoate, benzoylcarvacrol (carvacrol phenylurethane, m. p. 140°).

\begin{center}
\begin{tabular}{ccc}
(IV) Hypothetical stable Dihydroxide. & (V) $\alpha$-Glycol. & (VI) 1,4-Cineolic acid. \\
H$_2$C & C & H$_3$ \\
\hspace{0.5cm} & C & CH$_3$ \\
\hspace{0.5cm} & H$_2$C & H \\
\hspace{0.5cm} & H$_2$C & CH \\
\hspace{0.5cm} & C & C$_3$H$_7$ \\
& & & \\
(III) Erythritol. & & \\
H$_2$C & C & H$_3$ \\
\hspace{0.5cm} & H$_2$C & CH$_3$ \\
\hspace{0.5cm} & H$_2$C & OH \\
\hspace{0.5cm} & H$_2$C & CHO \\
\hspace{0.5cm} & C & C$_3$H$_7$ \\
& & & \\
(II) Conversion product. & & \\
H$_2$C & C & H$_3$ \\
\hspace{0.5cm} & H$_2$C & CH$_3$ \\
\hspace{0.5cm} & H$_2$C & OH \\
\hspace{0.5cm} & H$_2$C & CHO \\
\hspace{0.5cm} & C & C$_3$H$_7$ \\
& & & \\
(I) Ascaridole (Wallach). & & \\
\end{tabular}
\end{center}

**Oil of Levant Wormseed.** We have already stated that for some considerable time it has been impossible to procure this oil (*Oleum cinae*). It would appear that consumers are resigned to this fact, for we only very rarely receive enquiries for the article.

Wormseed oil is now hardly to be found in commerce, the reason being probably that the parent-plant (*Artemisia maritima*, L. var. *Stechmanni* = *A. Cina*, Berg, N.O. Composite), is not now distilled as it used to be, prior to being worked up for santonin.
The plant is found only in Russian Turkestan\(^1\)), and its habitat on the left bank of the Syr Daria is rather restricted. On the right bank, however, it is very widely spread, occupying the river-banks and plains between the large and the smaller rivers up to the Altai hills. The monopoly of collecting the flowers is leased out by the Government. The newly-opened flowers are richest in santonin, but as the plants flower very rapidly, the gathering, which usually takes place about the end of August, must be completed within a fortnight.

In common with all other wild plants, a considerable proportion of the *Artemisia* is collected every year by the inhabitants of the treeless steppes for fuel. That the herb has not been completely exterminated is only due to the fact that it is a perennial, and that before the gathering begins some of it has already reached such a degree of maturity that it sows itself. The numerous herds of sheep which graze in the district also destroy many plants. With careful management it would be possible to obtain a yield of from 150000 too 300000 poods (say 2415 to 4830 tons) of *Flores Cinex* per dessiatine (= about 2\(1/2\) acres).

**Wormwood Oil.** Our New York friends inform us that complaints are rife everywhere of sluggish sales, which is natural, seeing that the prohibition of absinth which has been enacted in several countries in the last few years has greatly restricted the demand for the article. For this reason the prices have receded somewhat, and they would doubtless be still lower than they are if there were no important stocks in second hand for which high prices were paid and which the owners are trying to sell by degrees, if possible without loss to themselves. We are of opinion that under the conditions now prevailing the cultivation of wormwood in the United States is certain to decline considerably. It is therefore all the more fortunate that our German wormwood oil is available to supply the world's requirements. Within the past few years this oil has found a market almost everywhere, and in view of its moderate price it is just as well suited to take the place of the American oil, as it was to make good the disappearance of the French oil, which formerly played such a considerable part. We have now struck French oil off our list for good.

**Wormwood Oil, Indian,** see p. 28.

**Ylang-Ylang Oil.** Our supplies of the finest oil ("Sartorius" brand) have come to hand with their customary regularity and were sufficient to cover the whole of the demand. The price may be described as firm; stocks are not accumulating, and lately there have been some rumours of difficulties in obtaining distilling material. Whether these difficulties are only temporary or whether we must prepare for a permanent falling-off in the supply we are as yet unable to judge, but in order to guard against surprises our friends among the consumers will be well-advised to contract in advance for their requirements, the oil to be delivered as called for. To all appearance there has been no check in the over-production in the island of Réunion to which we have referred on several occasions. Considerable shipments continue to be made from that island, most of them, it is said, to the European firm of which mention was made in our last *Report*.

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\(^1\) *Westnik finansow* **1912**, No. 33; *Pharm. Ztg.* **57** (1912), 778.
Novelties.

Oil from "Wild" Cardamoms. "Wild" Cardamoms, originally derived from Indo-China, of which the parent-plant was identified as Anomum globosum, Lour. (N. O. Zingiberaceae), when distilled yielded 4 p. c. of a colourless oil, which on examination was found to possess the following constants: $d_{15}' 0.9455$, $\alpha_d + 43^\circ54'$, $n_{D20}0 1.47141$, acid v. 0.8, ester v. 128.4, insoluble in 10 vols. 70 p. c., soluble in 1 vol. a. m. 80 p. c. alcohol. The constants of the oil show some similarity with those of the oil from "Ceylon cardamom seeds" (Report October 1910, 32) but the oil differs materially from the latter in respect of odour, in which particular it reminds rather of camphor oil; for which reason it is useless as a cardamom oil proper. The pronounced odour of camphor points to a considerable proportion of camphor, but as to this we were unable to determine anything definite, as our sample consisted only of a few cc. of oil.

Oil from Cherry stones. An oil which has recently been prepared by us from cherry stones was of interest in so far as up to the present it was an unknown product. For its preparation the stone was ground up with the shell, mashed up, and the paste, after being left standing for several hours, distilled with steam. By this process we obtained 0.016 p. c. of an oil possessing the following characters: $d_{15}' 1.0532$, $\alpha_d + 0^\circ$, $n_{D20}0 1.53888$, sol. in 2.5 vols. a. m. 60 p. c. alcohol. The hydrocyanic-acid content was 0.27 p. c. The oil was colourless to pale yellow and had an odour similar to that of bitter almond oil, although clearly differentiated from the latter.

Fennel Herb Oil. An oil distilled from fennel herb on the island of Jersey was sent to us some time ago for our opinion. The oil constituted a colourless liquid with an odour of estragon and was soluble in 5 vols. a. m. of 80 p. c. alcohol, with slight turbidity; $d_{15}' 0.9561$, $\alpha_d + 16^\circ 40'$. The oil only contains a very small proportion of anethol, but, judging by its odour, methylchavicol is an important constituent.

As we had at our disposal a sample of the raw material used for distilling, and, moreover, a supply of the fruit reached us afterwards, we were able to determine the botanical origin of the oil. Its parent-plant was Foeniculum vulgare, Miller.

Oil from the herb of Meum athamanticum. The herb of bald-money, Meum athamanticum, Jacq., an umbelliferous plant, which was collected in the neighbourhood of St. Andreasberg, in the Hartz Mountains, yielded upon distillation 0.88 p. c. of a deep reddish-brown oil with a celery-like odour. It was soluble in 3 vols. of 90 p. c. alcohol; $d_{15}' 0.9053$, $n_{D20}0 1.50327$; acid v. 8.8; ester v. 63.1. Owing to its dark colour it was impossible to determine the rotation of the oil. White crystals separated out from it, which at first melted between 83 and 84$^\circ$, and, after being once crystallised from alcohol, at 91$^\circ$. They may perhaps represent guajol. As only a very small quantity of the oil was at our disposal we have been unable to go further into this question.

On oil from the root of bald-money, see Gildemeister and Hoffmann, The Volatile Oils, 1st Ed. p. 568.
Chemical Preparations and Drugs.

"Agrumi" oils, Synthetic (Italian Essences). The exceptional advance in prices which the essences of Sicily and Calabria underwent during the winter, has naturally provoked an extraordinarily brisk demand for our well-tried artificial "Agrumi" oils. At times this demand was so strong that we were compelled to suspend further sales for longer or shorter intervals. Foremost among these preparations our synthetic bergamot oil enjoyed a popularity even exceeding our anticipations. We prepare this oil with an ester-content of about 38 p. c. and its cost is less than half of that of the natural oil containing about 35 p. c. of ester. It is mainly owing to the warm welcome extended to this preparation by consumers that the producers of the natural oil have been unable to raise their prices still further than they have actually succeeded in doing1). Certain of the raw materials needed for the preparation of our artificial bergamot oil have only been obtainable with difficulty and at advancing prices, owing to the sudden and important demand for them. On this account we have been obliged to raise our quotations for synthetic bergamot oil, but this has in no way restricted its sale. Judging by the favourable reports of the article which have reached us, we may count upon a large number of our customers turning permanently to the employment of this exquisite substitute, which is not subject to any speculative fluctuations in price, and it may be confidently expected that in future the Calabrian producers will find it difficult to dictate terms to their clients.

Synthetic lemon oil and synthetic orange oil have also been in brisk request, so much so that our factory was at times unable to keep pace with the demand. This is still the case with synthetic orange oil, and we shall therefore be unable to make offers of this article until the bulk of our contracts for delivery now in arrear have been executed. The extension of consumption of both these artificial products is naturally somewhat impeded by the fact that there are certain objections to their employment for alimentary purposes. These objections exist because as yet no official decisions are available as to the admissibility of the said products for such purposes. Neither of the two oils, however, contains any noxious constituents whatsoever, because their composition is modelled upon the constitution of the natural oils as scientifically established.

Aldehydes, Higher. These extraordinary far-going but at the same time extremely delicate odoriferous substances, which have found numerous devotees among the manufacturers of the finest perfumes, are well-known as one of our recent specialities. The manufacture of these articles is exceptionally difficult, for which reason we have not always been able to fill the demand. Moreover, we have recently been compelled to increase our prices considerably, because the previous quotations were not in consonance with the troublesome and costly process of manufacture. As is well-known, we supply the following higher aldehydes: octylaldehyde, nonylaldehyde, decylaldehyde, undecylaldehyde and duodecylaldehyde (laurinaldehyde). Particulars of these substances will be found in our Report of April 1912, pp. 142 and 143. We again advise all those of our friends who are not thoroughly versed in all branches of the art of modern perfumery, or whose sense of smell is not thoroughly trained, to abstain from employing these expensive and delicate preparations. We are therefore under the

1) See p. 53 of the present Report.
necessity of restricting the supply of free samples of these articles. The practice of selling them in 10 p. c. alcoholic solutions has so far proved suitable.

Almond Oil, pressed, from Almonds (German Pharmacopoeia V). In spite of the favourable crops which have been gathered in Sicily and Apulia, and of the comparatively slight demand for export, the prices have steadily risen within the last six months. It is reported that in view of the good prospects of the crop the exporters made numerous sales abroad without covering themselves, after which speculators took advantage of the purchases made to cover the commitments by driving up the prices. Girgenti-almonds of 1st quality, which were worth 195 L per 100 kilos last October, are now offered at about 220 L. Unfortunately quite lately rumours of repeated damage by frost have greatly unsettled the position of the market, especially because the possibility of further similar climatic influences will continue to exist for weeks to come. It would nevertheless be too early at present to draw any conclusions of the final result of the new crop. As a result the quotations for delivery after the new crop are very high, and we shall be compelled to follow suit with our quotations for pressed almond oil as soon as our cheap stocks are approaching exhaustion.

The cultivation of almonds in Sicily has been steadily assuming greater dimensions for some years past; the almond districts round about Girgenti having been much extended. We hear that not merely one variety of almond trees is being planted, but several bastard-species as well, which flower at different periods, so that the crop will henceforth not be so greatly dependent upon the weather during the flowering-period. This system is the more to be recommended because it contributes to equalise the average yield of the crop. It must further be borne in mind that those varieties of trees which owing to unfavourable weather during the flowering time yield none or little fruit that year, usually bear exceptionally well in the following year.

The increase of the production in recent years is well shown by the following figures, giving the quantities of almonds shipped from the port of Palermo:

<table>
<thead>
<tr>
<th>Year</th>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1907</td>
<td>530 tons</td>
<td>£ 590,000</td>
</tr>
<tr>
<td>1908</td>
<td>920 &quot;</td>
<td>1,150,000</td>
</tr>
<tr>
<td>1909</td>
<td>750 &quot;</td>
<td>1,290,000</td>
</tr>
<tr>
<td>1910</td>
<td>1,599 &quot;</td>
<td>2,530,000</td>
</tr>
<tr>
<td>1911</td>
<td>1,458 &quot;</td>
<td>2,100,000</td>
</tr>
</tbody>
</table>

Almond Oil, pressed, from Apricot Kernels. Notwithstanding the briskness of the turnover, the winter went by without bringing the advance in prices which, in our last Report, we designated as probable. We were able to cover our considerable requirements of apricot kernels at advantageous prices, and the war in the Balkans did not in any way affect the course of the market. So far it is impossible to say anything with regard to the prospects of the article.

Our informants in Syria send us the following account of the situation in the apricot kernel market there:

When the commercial relations between Turkey and Italy were resumed, it was generally hoped here that there would be an increased demand for apricot kernels on the part of the Italians, but this expectation has not been realised, because in the meantime those Italian buyers who purchase apricot kernels as comestibles (in which trade Italy plays a part of some importance) had become accustomed to Japanese and Chinese kernels, and were covering their requirements not only in Japan and China, but also in Morocco and Spain. As a result the demand has practically been altogether lacking, in spite of which the prices repeatedly
showed a little spurt, and at one time a basis-price of 65 £ cif Hamburg was reached. This figure, however, could not be maintained long, and finally the price receded to about 62 £ to 63 £, with occasional opportunities of buying even slightly below that limit. Although considerable parcels have been taken out of the market, partly for France and partly for Germany, a certain quantity is still left, but our farmers have been careful not to crack the stones of the remaining kernels, because the kernels keep best when protected by their shells, as in that case even prolonged storage does not deteriorate the kernels in any way. In view of the good state of preservation of the balance of their stocks from the last crop, the farmers in general have stuck to their prices, although certain concessions have been made when one or the other of them happened to be short of cash. At present the prices range from 61 £ to 62 £.

Benzoin. Up to the present **Styrax Benzoin**, Dryand. has been regarded as the parent plant of Siam-benzoin, but as a matter of fact (as we read in the *Kew Bulletin*) the drug is the product of **Styrax benzoides**, Craib. (N. O. *Styracaceae*), a species which has only recently been described. The tree is known to attain a height of from 36 to 45 feet, with a circumference of 3 feet. The benzoin-resin is collected by making V-shaped incisions in the bark, and flows into bamboo-receptacles affixed at the base of the tree. These receptacles are emptied every few weeks. The collection of resin usually takes place in the hot season. The resin is also frequently found in the bore-holes made by insects and occasionally at the foot of the tree-trunk.

A. Wichmann describes two varieties of benzoin which occur in Eastern Bolivia. They are there known by the names of *Estoraque* or *Benjui*, which signifies “storax” or “benzoin”. One variety of resin is derived from *Styrax Pearcei*, Perk. var. *bolivianus*, Perk. It exudes from incisions in the bark of the tree, congeals on the bark and is then removed. The sample examined by the author occurs in the form of irregular, oval, flattened pieces, of a grey, brown or reddish-brown colour, partly sticking together. Inside the sample yellowish to yellow almond-shaped pieces of varying size were observable. The resin was brittle; it fractured with a lustre as of glass or porcelain, and its odour reminded of benzoin and storax. It was completely soluble in alcohol and chloroform, partially soluble in ether. When heated in a test-tube white vappours were evolved, with an odour of benzoin and storax, and at the same time somewhat acrid. The mean acid v. of two tests was 96,6; sap. v. 195,15. The resin contains chiefly cinnamic and a little benzoic acid. The detection of the joint acids was most successful under sublimation in rarified air, carried out according to R. Eder’s method. The presence in the sample of vanillin (about 0,3 p.c.) was identified by the same method. This substance was identified by the colour-tests with phloroglucinol- and pyrogallol-hydrochloric acid among others. Wichmann also detected traces of an oil with a benzaldehyde-odour as well as of benzoresineol and of a resinotannol which shows no concordance with any of the hitherto-known resinotannols, and to which Wichmann has given the name of boliresinotannol. As the available resin-sample was very small it remains undecided whether styracin, benzene- and phenylpropyl cinnamate (bodies which are present in Sumatra-benzoin, to which the Bolivian resin bears a considerable resemblance) also occur in it.

Another resin, also collected in Eastern Bolivia, at Chiquitos, was derived from *Styrax camporum*, Pohl. Its colour was a brownish-yellow. As only traces of the

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resin were available all that could be determined concerning it was that it contained no cinnamic acid, for when heated with potassium permanganate it gave off no benzaldehyde-odour.

As Wichmann states in the introduction to his paper, similar resins are collected from *Styrax ferruginea*, Pohl (S. Pohlii, A. DC.), a native of Brazil, and from *S. ferruginea* Nees et Mart. (*S. reticulata* Mart.), *S. aurea*, Mart. (*Pamphilia aurea*, Mart.) and *S. nervosum*, A. DC.¹)

**Borneol.** From a communication in an English periodical we gather ²) that in Japan, in lieu of the natural Borneo camphor (*Taisei Rianjo*), synthetic borneol, imported from Germany or France, is frequently used. Up to the present the import duty on borneol was about 3 yen, and that on Borneo camphor 6 to 7 yen per kin, but in the revised Customs Tariff the duties on imported borneol have been raised. This fact will no doubt be of advantage to the Japanese borneol industry, which hitherto has not greatly competed with the imported article. The imports into Japan of Borneo camphor, Ngai-camphor, and borneol were as follows:—

<table>
<thead>
<tr>
<th>Year</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1909</td>
<td>14234 Kin</td>
</tr>
<tr>
<td>1910</td>
<td>35798 &quot;</td>
</tr>
<tr>
<td>1911</td>
<td>45199 &quot;</td>
</tr>
<tr>
<td>1912 (first 6 months)</td>
<td>7947 &quot;</td>
</tr>
</tbody>
</table>

**Cinnamic Alcohol.** We are now in a position to supply this preparation, for which the demand is so great in the perfumery trade, on very advantageous terms, as we have enlarged our manufacturing plant. We call attention to the reduced quotation in our price-list.

**Coumarin.** Since the regulation of the selling-prices by a Syndicate, the trade in this article takes its course without noteworthy fluctuations, but the Syndicate has at any rate established more wholesome conditions of business, which have saved the article from utter ruin. In the export-trade, however, underselling is still of frequent occurrence, the Swiss manufacturers of synthetics being specially prominent in soliciting orders at prices and conditions which exclude any consideration of profit.

**Eucalyptol.** The scarcity of eucalyptus oils containing eucalyptol, concerning which we report on another page, has of course greatly stimulated the sale of our pure eucalyptol. Although we still dispose of very considerable supplies of cheap raw material, the tightening of prices is of course only a question of time, and we earnestly advise our regular customers not to forego the opportunity which still exists of covering their requirements cheaply.

**Geraniol.** It is hardly necessary to point out that the high prices of geranium oil have stimulated the trade in geraniol to an extraordinary degree. Our works are now in a position to supply large quantities regularly, and it is therefore hardly possible that such delays in delivery as sometimes took place last year, much to our regret, will occur again.

¹) According to the *Index Kawensis*, *Styrax nervosum*, A. DC. is synonymus with *S. ferrugineum*, Nees et Mart.

²) *Chemist and Druggist* 81 (1912), 477.
Heliotropin. We have considerably extended our manufacturing plant, and are therefore at last in a position to supply the requirements to the fullest extent, after having in the past been mostly in arrear with our output. Our heliotropin is distinguished by its exceptionally pure heliotrope-арoma from other brands, which often have a certain chemical odour that forms an obstacle to their employment in better-class perfumes.

Linalyl Acetate. On p. 122 of our last Report we quoted a case showing that certain firms occasionally supply very inferior products under the description of linalyl acetate, and in the course of the last half-year we have several times had an opportunity of making the acquaintance of such “cheap” preparations, for it does not require any special argument to establish the fact that one of the results of the high range of prices of bergamot oil was an unusually brisk demand for linalyl acetate. Of nine samples which were sent to our laboratory for our opinion not a single one really answered the requirements; all contained besides linalyl acetate a varying proportion of other esters (geranyl acetate, terpynyl acetate), a few also contained a little terpene. These are all compounds which may occur as by-products in the course of manufacture of the ester. In one instance the odour of the sample was rather that of geranyl acetate than of linalyl acetate. Moreover, in a few of the samples the ester-content was as low as 60 p.c., which alone would be sufficient to indicate inferiority.

Fractional distillation affords the best means of judging the quality of linalyl acetate, of the remaining constants only a very few are occasionally valuable. For instance: the estimation of the ester value gives a general clue to the ester content, but of course it does not indicate what proportion of that ester content is represented by linalyl acetate. On the other hand, if fractional saponification reveals considerable differences in value1), it is fair to suspect the presence of terpynyl acetate, but these constants are of no use if, with a normal ester content, linalyl acetate is accompanied by a still larger proportion of geranyl acetate. Fractional distillation, however, as we have again established, is invariably useful, because any esters which may be present as contaminations in the linalyl acetate have higher b. p. than the last-named product and can easily be detected if the fractionation is properly conducted. 80 p.c. linalyl acetate which is free from these foreign esters, and which besides linalyl acetate contains only linalool, does not boil above 99° at 11 mm. press.

We again wish to point out that the preparation which is manufactured and brought into commerce by us, consists exclusively of linalyl acetate and linalool, and contains an average proportion of 80 p.c. of the former. A comparison of its odour with that of cheaper commercial brands will suffice to convince any expert of the superiority of our linalyl acetate, of which the price is much more nearly related to its true worth than is the price of the “cheap” merchandise.

Menthol. In accordance with our custom we deal with this article under the heading “Peppermint oil, Japanese,” see p. 80.

Peru Balsam. This important article has been maintained without alteration at the former high prices, which will no doubt also continue to rule for the future, as the supplies are only just equal to the requirements and there is no possibility of

1) In the case of a pure 80 p.c. linalyl acetate this difference may be as much as 5,8. On the carrying out of the process of fractional saponification see Report October 1911, 116; October 1912, 122.
any accumulation of stocks in the principal markets. It is further said that the export-duty from the producing country has lately been raised again, a circumstance which naturally contributes to make the prices still dearer.

H. R. Jensen\(^1\) recommends that in testing Peru balsam analytically the iodine value of its cinnameine shall also be estimated, and that furthermore the rotation of the initial 30 p.c. which pass over in the distillation of cinnameine shall be determined. Cinnameine from pure balsam gave an iodine value of 23.8, whereas that isolated from a synthetic product only gave 1.5. Distillation in vacuo (with a three-bulb flask) of a cinnameine from synthetic balsam only gave inactive fractions, whereas of cinnameine from natural balsam the initial 10 p.c. had rotation +5°40', the second 10 p.c. +1° and the third 10 p.c. +0°15'. Jensen believes that the distillation can also be conducted under ordinary pressure.

Another balsam which was examined at the same time, and of which the cinnameine was markedly rich in cinnamate was in Jensen's opinion probably adulterated with storax.

Pollantin. Judging from authoritative expressions of opinion, and from our own experience, Pollantin-ointment, the new form of applying Pollantin, which was first placed on the market by us in the year 1912, has been everywhere well received. In almost all cases which have come to our knowledge, patients who, for whatever reason, abstained from using the older Pollantin-preparations, have willingly taken to the salve and have found in it a means of successfully combating hay-fever.

We may also take this opportunity of referring once more to the Pollantin-tablets of which we first made mention in our Report of April 1912. We prepared these tablets on the advice of Prof. Dunbar as a remedy for the exceedingly tormenting asthmatic troubles which afflict many patients in the later stages of hay-fever. The tablets consist simply of Pollantin-powder levigated with sugar of milk, and (with the exception of a neutral binding-material) they are free from any alien substance. We have had nothing but good reports of their efficacy last year. Before placing these tablets upon the market, we again desire to call the attention of the medical profession to this remedy, of which the mode of application is extremely simple, and of which we shall be pleased to supply samples for experimental purposes.

We also wish to point out once more to our customers, and in particular to the pharmacists among them, that we are prepared to exchange old tins of liquid Pollantin bearing control-numbers from 161 (inclusive) downwards for fresh serum, and we therefore request them to look out such numbers from their stock and return them to us. Upon receipt the new tins will be forwarded immediately. Powdered Pollantin, if properly stored, has unlimited keeping quality, and for that reason, as we have repeatedly stated, we cannot undertake to exchange it.

After laborious experiments extending over several years, we have succeeded in producing a UNIFORM SERUM, suitable for SPRING as well as for FALL Hay Fever and kindred troubles. Beginning with the coming season we shall, therefore, put up Pollantin, powder as well as liquid, in a single style of packing only, thus obviating the possibility of mistakes which, it would appear, happened occasionally, such as patients receiving Fall serum when requiring Spring serum, and vice versa.

\(^1\) *Pharmaceutical Journ.* 90 (1913), 210, 276.
 Needless to say, this innovation applies only to the United States, for which country two distinct kinds of serum had to be made *ab initio*, seeing that there are two distinct Hay Fever complaints, caused by entirely different plants. In England and on the Continent, however, the serum will be the same as hitherto, inasmuch as only one style of serum was used here ever since Pollantin was first introduced, there being no necessity for two distinct kinds, as Europe is blessed with the ordinary variety of Hay Fever only.

Another novelty will be placed definitely on the market this year, *viz.*, our POLLANTIN SALVE. This is a simple trituration of Dr. Dunbar's Hay-Fever serum Pollantin (powdered) with a slightly scented, mild and neutral, oleaginous base. It appears to be more especially indicated in cases where, for several reasons, the ordinary form of Pollantin, powder as well as liquid, is not tolerated by hyper-sensitive patients. In such cases it is advisable to use the Ointment (Salve) preferably prophylactically, particularly so for nasal symptoms. Full instructions for use are given in literature accompanying every package.

O. Kammann¹), the well-known collaborator with Dunbar, has published an extensive paper on pollen-toxin (the agent which causes hay-fever), and its principal characteristics. Kammann propounds the question to what extent the toxic properties of pollen antigens are affected by the presence of protective ferments, lipoids and substances akin to, or derived from, albumen. He leaves it an open question whether toxic action is set up by a body which is free from albumen or by one which responds to a limited extent to reactions for albumen, or by a concatenation of this body with lipid substances (lecithin) or with proteines, as in the older conception of the toxalbumins. As Kammann points out, in the experimental solution of this question considerable difficulties have been encountered, partly owing to the labile character of the bodies concerned, and partly because of our still very imperfect knowledge of their chemical structure. Hence, where chemical methods of resolution fail, recourse must be had to the more subtle biological methods in order to determine whether it is possible for a body which has been purified by chemical manipulations to possess at one and the same time several properties (toxic, hæmolytic, and fermentative). Applied to pollen-toxin, these considerations resulted first of all in an improved method of preparing the toxic principle, by extracting the broken-up pollen with distilled water instead of, as previously, with a solution of common salt, in order to obviate the entering into solution of the physiologically inactive globulines. With the object of destroying the starch which has been dissolved out, and which is extremely detrimental to the biological behaviour of the toxin, the pollen-solution is treated for several hours with diastase-solution at 37°, left to stand for 24 hours in a refrigerator, placed in a centrifugal machine, and precipitated with alcohol in the familiar manner. In the course of this manipulation the enzymes are precipitated with the toxin. The precipitate is quickly filtered, and the last traces of alcohol are driven off at room-temperature in an apparatus constructed for the purpose, by passing-over a current of dry air. The substance is now again dissolved in distilled water and the albumens are left to be digested by the proteolytic ferments which are also present, an operation which takes place in the course of several days' standing in a refrigerator. After this manipulation there results at last a preparation which occurs in the form of yellowish, silky-lustrous scales, and which still responds to the biuret-test, but not to Millon's or to Molisch's reactions.

¹) Biochem. Zeitschr. 46 (1912), nos. 1 and 2. From a copy kindly sent to us.
This purified toxin often proved a hundred times more efficacious with hay-fever patients than did the older form of preparation, and when given to animals as an intravenous injection, the purified preparation showed an extraordinary increase on previous experience in the rapidity with which ant-bodies were formed.

Kammann subsequently carried out further experiments with the object of again identifying, more sharply than before, the ferments which have been found to exist in the pollen of rye. By this method he was able to detect the presence of protease, diastase, dextrase, catalase and lipase. Lecithinase, tyrosinase, and lactase were absent.

Compared with the action of rye-pollen in exiting hay-fever, the other toxic principle (the hæmolytic) is of less practical importance. Kammann has ascertained that the substance which dissolves the blood-corpuscles is much more sensitive towards chemical and physical influences than is the principle which causes hay-fever. It is considerably weakened by proteolytic ferments, and is destroyed by heat. Its presence may be detected by saturation with a deposit of purified blood-corpuscles, a toxin being then left behind which is solely capable of causing hay-fever. As is the case with the poison of snakes, spiders, etc., the hæmolysin only becomes active in the presence of lecithin or similar lipoids. This fact has been established by quantitative experiments by binding amboceptors. Since it has been found that toxin dissolves the blood-corpuscles of hay-fever patients much more rapidly than it dissolves those of normal subjects, Kammann inclines to the view that in the blood of normal individuals lecithin is so firmly combined as to be incapable of grappling with the hæmolysin and combining with it, for which reason it is incapable of causing hæmolysis. But in the case of hay-fever patients it is held that lecithin is present in the blood in the form of a somewhat loose combination, easily split-up, whereby it is enabled to combine with the hæmotoxin and thus to cause hæmolysis. The blood-serum of several animal species possesses the activating action of lecithin-solution, but in a still stronger measure, although in a different degree.

It is well-known that in the course of time several writers have denied to the hay-fever poison the character of a true toxin (i.e. a toxin capable of producing antitoxins). Recent experiments by Dunbar however, to which we have referred on a previous occasion 1) have established the correctness of the older view. Further evidence in this direction is afforded by experiments which have been carried out in the Institute of the well-known clinician, Sir Almroth Wright, by two of his assistants, Noon 2) and Freeman 3). These investigations have resulted in the widespread adoption of a new mode of treatment of hay-fever. The authors in question have administered hypodermic injections of pollen-toxin solutions to hay-fever patients whose sensitiveness had been quantitatively estimated by the ophthalmo-reaction. The treatment was administered in the autumn and winter, that is to say during the season of immunity from the complaint, the remedy, which was prepared from the pollen of Phleum pratense, L., being given in increasing doses. In a considerable proportion of cases the condition of the patients in the succeeding hay-fever season showed a marked improvement. This improvement manifested itself in the alleviation of the symptoms generally, and it was capable of being measured by the ophthalmo-reaction, which showed a considerable reduction in sensitiveness after treatment. Our Pollantin-treatment therefore represents a passive immunisation (parallel in many instances,

according to Albrecht's statements, with an active immunisation), whereas the new treatment in which the hay-fever toxin is hypodermically injected by the medical practitioner in carefully chosen increasing doses and at the proper season of the year, represents the active form of immunisation. In Germany this treatment has been tried by Ellern and others, whose results showed a more or less pronounced improvement in the majority of cases. Nevertheless, all the patients thus treated did contract hay-fever, although some of them only had mild attacks. But seeing that in the year 1912 patients who had not been treated by the new method, likewise suffered in a lesser degree than in previous years, it is impossible as yet to pronounce a final judgment on the merits of Wright's inoculation-method.

Rose "Schimmel & Co." (Moss Rose). The great popularity which has been extended to our speciality known as "red rose" in all expert circles has naturally afforded us an inducement steadily to continue our investigations in the domain of rose-scents with a natural basis. We have now placed upon the market an outcome of these researches in the shape of a new product known as "Rose 'Schimmel & Co.' (Moss Rose)". In taking this step we feel firmly convinced that to the series of rose-aromatics at the disposal of the modern perfumer, desirous of reproducing the scent of roses either in the form of an alcoholic or a non-alcoholic preparation, we have added an article which must impress everyone who will try it carefully, by its delicacy, the peculiar cachet of its aroma, and its fidelity to Nature. We may again lay stress upon the fact that the natural basis of this article consists of the natural extract (prepared by a special process) of our German roses grown here near Miltitz, and that it is thereby favourably differentiated from competing productions bearing similar names. We shall be glad to supply samples of this interesting novelty. No one who is desirous of discovering really exquisite bases for modern rose-scents could find more suitable preparations for this purpose than our two varieties of Rose "Schimmel & Co."

Rose "Schimmel & Co." (Red Rose). We should be repeating ourselves too often if we were again to give prominence to a description of the virtues of this aromatic substance, which we have already praised on several occasions, and which has made furore in all perfumery circles at home and abroad. Our sales of this exquisite synthetic scent with a natural basis are incessantly growing, and this is the most convincing proof that our repeated encomiums of the article, although to some of our readers they may have appeared a little overdone, have in reality not been too far-fetched.

Safrol. Business in this article has again been very brisk. Cheaper raw material having come to hand, it was possible again to reduce the prices somewhat, but they have now reached a level which we may fairly describe as in all probability a stable one. Our output is so great that we are able to deliver immediately any desired quantity.

Tolu Balsam, which was so scarce last year, has gradually receded to a reasonable limit of value under the pressure of plentiful supplies. Quite lately the downward movement has received a check and we scarcely think that the prices will fall still further.

Vanillin. In view of the prevailing depression in price and the bitterness of the competition, there is probably no one who derives any particular satisfaction from trading in this article, the more so because the raw material has recently become dearer and dearer. We make it a practice to abstain from competing whenever we are unable to secure at any rate a very modest profit. In the year 1890 the price of vanillin was 800 M; in 1900 it was 100 M per kilo. Tempi passati!

In the flowers of Gymnadenia albida, Rich. (N. O. Orchidaceae), collected at Davos, E. O. von Lippmann1 has detected the presence of vanillin. The flowers have a pronounced odour of vanilla. von Lippmann cut the already faded flowers into small pieces, in the course of which manipulation the aroma given off was perceptibly increased, perhaps as a result of the splitting-up of a glucoside. He then extracted the substance with alcohol and ether and dried the solution after precipitating it with sugar of lead. An ointment-like substance of the most exquisite aroma remained behind, from which vanillin (m. p. 82°) was isolated. The vanillin, when dissolved with ferric chloride, assumed a beautiful blue colour and yielded the characteristic barium compound (C₈H₇O₃)₂Ba.

1) Berl. Berichte 45 (1912), 3432.
Notes on Scientific Research in the Domain of the Essential Oils.

General.

From the *Mitteilungen zur Geschichte der Medizin und Naturwissenschaften* we gather that in the papers left behind by the Swedish chemist, the late L. F. Svanberg, two hitherto unpublished letters from Fr. Wöhler to Berzelius have been discovered. The letters, which were written in the year 1848, contain, in addition to vivid descriptions of those times of political unrest, a few interesting scientific data concerning research in which Wöhler was engaged at that time. The first of the letters, which is dated March 8th 1848, contains the following passage:

"I will also send thee shortly a dissertation on so-called turpentine-camphor; a truly beautiful work, which has been carried out in my laboratory by Herr List. In this investigation a really remarkable example of catalysis was shown. When turpentine-camphor \( C^{20}H^{30}O^4 \) is warmed up with any acid it is converted into a volatile oil, with a perfect aroma of hyacinths, which is \( C^{20}H^{17}O \). It appears that one single drop of acid is capable of converting endless masses of camphor."

[Ebenso werde ich Dir in Kurzem eine Dissertation über den sogenannten Terpentincampher schicken, eine recht schöne Arbeit, die Hr. List in meinem Laborat. ausgeführt hat. Es hat sich dabei ein recht merkwürdiges Beispiel von Katalyse gezeigt. Wird nämlich der Terpentincampher \( C^{20}H^{30}O^4 \) mit irgend einer Säure erwärmt, so verwandelt er sich in ein vollkommen wie Hyacinthen riechendes flüchtiges Öl, welches \( C^{20}H^{17}O \) ist. Ein einziger Tropfen Säure scheint unendliche Mengen Campher verwandeln zu können.]

The research to which Wöhler here alludes is the familiar investigation "on so-called turpentine oil hydrate", which was published by C. List in *Liebig's Annalen* in that same year. The essential oil which List obtained from terpin by heating with dilute sulphuric acid, to which he gave the name of terpinol was, as we now know, a mixture of terpenes and oxygenous constituents. Both scientists thought that their preparations gave off an odour of hyacinth, a belief which is probably due to the lilac-like odour of terpineol.

There has recently been published the concluding part of the late W. Mitlacher's work on experiments in the cultivation of medicinal plants, to which we referred on p. 128 of our last Report.

An article which has appeared in the *Perfumery and Essential Oil Record*, vol. 3 (1912), 242, refers to the experiments in the cultivation of odoriferous plants which have been made at Donolly (Victoria). A geranium oil distilled in this district possessed the following characters: \( d_{180} 0,906 \); \( \alpha_0 — 14,25^\circ \), so-called total geraniol 51,8 p. c. Distillation on a large scale has never yet been attempted at Donolly.

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Still-room A at Schimmel & Co.'s Works, Miltitz near Leipzig.
Great results are anticipated from the cultivation of geranium and lavender in Mexico. Dolley is of opinion that the natural conditions in that country are exceptionally favourable to the production of odoriferous plants.

At a meeting of the Royal Commission on Resources and Trade of the Dominions\(^1\), at which the possibility was discussed of cultivating aromatic plants in various parts of the British Empire, a brief reference to the abovementioned experiments was also made by one of the experts present.

In a contribution on the chemistry of essential oils, Augustín Murúa y Valerdi\(^2\) discusses the syntheses of their constituents. He also, in numerous tables, passes in review the majority of the bodies which have been found to exist in essential oils, giving the structural formula, the natural distribution and the constants of each compound. The author concludes his article with the following passage:

"In 1901 France exported essential oils to the value of over 11 000 000 francs, Germany to the value of over 8 000 000 marks, the United States for over 5 000 000 francs, Japan (in the year 1907) over 10 000 000 marks' worth of camphor, Bulgaria (in 1908) 2 000 000 marks' worth of rose oil, and the Philippines ylang-ylang oil to the value of 2 203 600 pesetas. In view of such figures it is incomprehensible why Spain has remained so backward in an industry for which its soil and climate are so exceedingly suitable; it would seem as if our capitalists had exhausted themselves in the manufacture of textiles and beet-sugar. If I should succeed, by this publication, in drawing your attention to a source of revenue of such importance for the welfare of our nation, my efforts will not have been in vain. But the fact should not be lost sight of that scientific work must always precede industrial and commercial activity; that it is in our High Schools that the foundations are laid for a truly progressive and independent national industry, and that so long as these schools, owing to their bureaucratic character and the general indifference of the nation, remain unfruitful, the efforts of our educated classes will remain vain and our industry will remain restricted to the limits of our own country, unable to compete in the markets of the world. So long as these conditions persist we shall not reconquer the glorious part which belongs to us and which at one time we played upon the world's stage."

J. C. Umney and S. W. Bunker\(^3\) have continued their investigations into the solubility of water in essential oils. They took essential oils saturated with water as well as dry essential oils, placed them both in completely-filled and in half-filled bottles, and kept them for six months, some in the dark and some exposed to daylight, the constants of the dry and of the wet oils being estimated both before and after keeping. The following oils were examined: nutmeg, juniper berry, lemon, orange, sandalwood, savin, citronella (Ceylon and Java), palmarosa, lemongrass, cassia, cinnamon leaf, clove, and thyme. Generally speaking, the sp. gr., rotation and refractive index of the terpene oils undergo a change in keeping. The alcohol-content is somewhat reduced by storage, the difference being more clearly expressed in the case of the wet than of the dry oils. As regards the oils containing aldehydes, it is impossible to draw up any generally applicable rules. Of the oils containing phenols, those which had been kept in daylight showed the greatest increase in sp. gr. and refractive index.

\(^1\) Chemist and Druggist 81 (1912), 643.  
\(^2\) Memorias de la Real academy de ciencias y artes 10 (1913), No. 16.  
\(^3\) Perfum. and Essent. Oil Record 3 (1912), 325; 4 (1913), 4, 38; Report October 1912, 128.
Bibliography.

We may here refer to an illustrated article by F. Rochussen\(^1\) in which the author, in an unconventional form, gives a brief sketch of the genesis of the chemistry of odoriferous substances and of the working-methods at present applied in that branch.

Two articles by A. Reclaire, which have appeared in the Chemiker Zeitung [36 (1912), 1125, 1150, 1161] and elsewhere\(^2\), deal with progress in the domain of the chemistry of the terpenes, essential oils and aromatic substances.

Analytical Notes.

On p. 45 of the present Report we present the results of our experiments in the determination of certain aldehydes and ketones by the phenylhydrazine method.

Jeancard and Satie\(^3\), together with Umney and Parry\(^4\), declare themselves in favour of the unification of processes for commercial analysis and valuation of essential oils and odoriferous compounds. Their object is to remove misunderstandings and contradictions in the evaluation of the products in question. Umney and Parry have communicated details on the subject before the International Congress of Applied Chemistry which was held in New York last September. In addition to physical tests, they attach importance above all to chemical methods of determination, and of the latter they adduce a number of examples, such as the determination of aldehydes, phenols, esters, and alcohols. For aldehyde estimation they suggest the bisulphite method, which is objected to by Hill and Cocking\(^5\), who prefer estimation with neutral sulphite.

It remains to be seen what measure of success will attend the efforts of Jeancard, Satie, Umney, and Parry. We do not intend to express ourselves with regard to the separate proposals until the matter has assumed a more definite shape.

B. G. Feinberg\(^6\) has subjected the various methods of estimating aldehydes to control-tests, taking for this purpose six typical aldehydes, viz.: formaldehyde, benzaldehyde, salicylic aldehyde, \(p\)-hydroxybenzaldehyde, anisic aldehyde, and vanillin. Feinberg gives the following method for estimating benzaldehyde by the bisulphite method: About 25 cc. of a 1 p. c. benzaldehyde solution is diluted in a stoppered flask with 25 cc. of about 3 p. c. bisulphite solution. After 25 minutes the excess of bisulphite is titrated back with iodine and starch-solution as an indicator. A blank test is carried out simultaneously. The difference between the quantities of iodine consumed in both cases corresponds to the quantity of aldehyde employed. 1 gram iodine = 0,41178 grams benzaldehyde, 0,11858 grams formaldehyde, 0,48081 grams salicylic aldehyde, 0,5360 grams anisic aldehyde, and 0,5990 grams vanillin.

The sulphite method only gave good results in the case of benzaldehyde. About 1 gram benzaldehyde is dissolved in 10 cc. alcohol in a well-closing flask, the sides of the flask being rinsed out if necessary with about 10 cc. water, in order to remove any drops adhering to them. The solution is thereupon neutralised with decinormal alkali liquor, with the addition of 6 drops 1 p. c. phenolphthaleine solution; 50 cc.

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neutral sodium sulphite solution (about 20 p.c.) is added and the whole titrated with seminormal sulphuric acid until the red colour has disappeared. At the same time a blank test should be made and the acid used up deducted from the quantity of acid which is required for the determination of the aldehyde. The quantity of alkali consumed in neutralising the aldehyde is converted into the corresponding quantity of benzoic acid and the latter deducted from the quantity of benzaldehyde which has been used. This method gave a result of about 99 p.c. benzaldehyde. The method is however a complete failure with salicylic aldehyde and vanillin, with anisic aldehyde the results obtained were too low. The calculation is made according to the following equation: 
\[ R \cdot \text{CHO} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = R \cdot \text{C(OH)}\text{NaHSO}_3 + \text{NaOH} \]

The method proposed by J. Hanuš for estimating vanillin, by precipitating as \( p \)-bromophenylhydrazone, was also found to answer with anisic aldehyde.

Feinberg obtained good results when estimating the aldehydes as \( p \)-nitrophenylhydrazone by the method of W. Alberda van Ekenstein and J. J. Blanksma\(^1\)). In the case of benzaldehyde he proceeds as follows: 25 cc. of a 1 p.c. benzaldehyde solution (in 12 p.c. acetic acid), is diluted with 50 cc. water and mixed with 30 cc. of 30 p.c. acetic acid containing double the calculated quantity of \( p \)-nitrophenylhydrazone. After 5 hours the precipitate is filtered in a Gooch crucible and washed out with 10 p.c. acetic acid until a well-defined coloration has ceased to ensue upon the addition of alkali. The precipitate is then dried at 105 to 110° and weighed. The benzaldehyde-content is found by multiplying with 0.44. Here also it is necessary to ascertain by titration the quantity of benzoic acid which is present in the benzaldehyde, and to deduct it from the quantity of benzaldehyde used. The average proportion of benzaldehyde found was about 99 p.c. The same prescription applies to salicylic aldehyde, but in this case filtration may be commenced after 1 hour (factor 0.4747).

For vanillin and anisic aldehyde Feinberg gives the following prescription: Dissolve 0.5 gram aldehyde, if necessary in a little alcohol and acetic acid, and after diluting with 75 cc. water and warming, mix the solution drop by drop with constant stirring with a solution of \( p \)-nitrophenylhydrazone in double-normal hydrochloric acid. Filter after 30 minutes in a Gooch crucible and wash out with double-normal hydrochloric acid and afterwards with water until only a faint opalescence is produced by silver nitrate. For the estimation of the anisic aldehyde content use as factor 0,50188, for that of vanillin, 0,5353.

The results obtained by the various methods are summarised in the table below:

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>92,02 to 95,19</td>
<td>97,31 to 99,09</td>
<td>91,12 to 93,55</td>
<td>98,12 to 99,42</td>
</tr>
<tr>
<td>Salicylic aldehyde</td>
<td>80,04 „ 82,23</td>
<td>indeterminable</td>
<td>93,04 „ 94,35</td>
<td>94,40 „ 95,42</td>
</tr>
<tr>
<td>Anisic aldehyde</td>
<td>89,90 „ 90,40</td>
<td>92,33 to 94,90</td>
<td>99,09 „ 99,50</td>
<td>99,70 „ 100,25</td>
</tr>
<tr>
<td>Vanillin</td>
<td>94,81 „ 95,77</td>
<td>indeterminable</td>
<td>98,50 „ 99,37</td>
<td>99,77 „ 100,52</td>
</tr>
</tbody>
</table>

The constants of the aldehydes examined were as follow:

Benzaldehyde . . . B. p. 112,5 to 113° (100 mm.),
Salicylic aldehyde „ 166 to 166,5° (360 mm.), 139 to 139,5° (100 mm.),
Anisic aldehyde . „ 195 to 195,5° (205 mm.).

\(^1\) Recueil trav. chim. des P.-B. 24 (1905), 33; Chem. Zentralbl. 1905, l. 1277.
J. C. Umney and C. T. Bennett have made experiments in the quantitative acetylation of citronellal, and have found, in confirmation of the earlier investigations conducted by us, that accurate results are obtained from a period of acetylation extending over two hours if 2 grams of anhydrous sodium acetate are used for 10 cc. of oil. According to the results obtained by the English chemists, it is a matter of indifference whether 10, 15 or 20 cc. acetic anhydride are used. But if under otherwise equal experimental conditions a larger proportion of sodium acetate is used, the results obtained are too high in proportion to the greater quantity of sodium acetate employed. When using 2.5 grams sodium acetate to 10 cc. oil and acetic anhydride we (loc. cit.) had obtained 103.8 and 104.4 p.c. citronellal, whereas Umney and Bennett obtained as much as 109 p.c. when acetyling with 10 cc. citronellal, 20 cc. acetic anhydride and 5 grams sodium acetate.

J. Allan and C. W. Moore have carried out a series of similar estimations. They found that in the case of geraniol (10 cc.), varying proportions of acetic anhydride (10, 15 and 20 cc.) and sodium acetate (1, 2 and 3 grams) did not affect the quantitative result of the acetylation whereas in the case of citronellal, according to the experimental conditions, divergent values were obtained. From the results as set forth in table-form (although these results are in part mutually contradictory and therefore do not admit of the formation of an entirely positive judgment), so much at any rate may be concluded that, generally speaking, concordant results are obtained when for two hours' acetylation from 10 to 15 grams acetic anhydride and 2 grams sodium acetate per 10 grams citronellal are used.

O. Tunmann calls attention to the fact that among the bodies which occur in resins, cinnamic acid affords the most beautiful sublimates, and that this property may be utilised with advantage for its detection by microchemical means. He gives the following method for microsublimation: On an asbestos-slab measuring $12 \times 12$ cm., by 2 mm. thickness, place a small piece of a recipient, upon which place the substance under examination. At a distance therefrom of from 2 to 3 cm. on the asbestos-slab is a small wooden stick, 3 to 4 mm. high and from 6 to 8 cm. long. A recipient for the sublimate is now placed over the substance under examination in such a way that one end rests upon the asbestos-slab and the other upon the wooden stick, care being taken that the recipient does not touch the lower piece of glass. When these conditions are observed the sublimation-space measures from 1 to 1.5 mm. in height. The asbestos slab rests upon an iron ring. Heat is conveyed by means of a spirit lamp of which the flame just touches the underside of the asbestos slab, and which can be held from 2 to 5 cm. high as required. After the commencement of the heating the recipients must be frequently changed, because otherwise, owing to the gradually increasing heat of the recipient, an escape of the sublimation-vapours is to be feared. The length of the wooden stick is of importance in order to make easy the exchange of the glasses.

Cinnamic acid readily sublimates upon the asbestos slab without decomposition. The crystals begin to separate out after a short time and polarise vigorously. They consist mostly of very characteristically shaped leaflets, several of which are often found grown together. When a drop of potassium permanganate solution is added

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1) Perfum. and Essent. Oil Record 3 (1912), 251. — 2) Report April 1910, 156. — 3) Perfum. and Essent. Oil Record 4 (1913), 13. — 4) Only from 84.7 to 85.6 p.c. was obtained, probably because the preparation was not quite pure. — 5) Pharm. Zentralh. 54 (1913), 133. — 6) Apotheker Ztg. 72 (1912), 497, 507.
the sublimate, when heated, develops an odour of benzaldehyde. In testing, regard is to be had to the fact that the resins often contain benzoic acid in addition to cinnamic acid. Where benzoic acid is present, it is found in the initial sublimates; the cinnamic acid passing over at a later stage. Moreover, the benzoic acid crystals are very definite in shape and under polarised light their complex is different from that of cinnamic acid crystals. Among chemical differentiations Tunmann mentions the different behaviour of the two acids towards silver nitrate and towards bromine vapours. When silver nitrate solution is added, the greater part of the crystals of cinnamic acid enters in solution, or they become insignificant and lose their magnificent colours under polarised light. Benzoic acid, it is true, also dissolves, but it soon reappears in more pronounced, vigorously polarising crystals of silver benzoate. The action of bromine vapour converts cinnamic acid into dibromo cinnamic acid; upon benzoic acid it has no effect.

Further examination is needed to ascertain to what extent the esters of cinnamic acid are also found in the sublimates, and whether they occur in them in the crystalline form.

Some time ago (Report October 1910, 61; April 1911, 149) we described a method for the quantitative estimation of glyceryl acetate in essential oils which consists in shaking out 10 cc. of the oil under examination with 20 cc. of 5 p.c. alcohol and of saponifying 10 cc. of the filtered alcoholic-aqueous liquid after the two layers had separated, and after previously neutralising with 5 cc. seminormal potash liquor. If glyceryl acetate is absent not more than 0,1 cc. seminormal potash liquor is used up. M. S. Salomon and W. M. Seaber¹) have experimented with this method on bergamot oil to which glyceryl acetate had been added and have found, in confirmation of our previous results, that even 2 p.c. glyceryl acetate may thus be detected without difficulty, although at the same time it was found that even after shaking out five times with dilute alcohol the whole of the glyceryl ester had not been removed from the oil.

On the other hand another method²) which has been recommended for the same purpose proved to be entirely useless. This method is based upon the fact that glyceryl acetate volatilises with difficulty, and draws the conclusion of an eventual sophistication of the bergamot oil under examination from the saponification value of the evaporation-residue. The limits of value for normal oil were given as 145 and 190. By this method Salomon and Seaber were unable to detect even 5 p.c. of triacetin in a sample of bergamot oil. Although, after the addition of the triacetin the sap. v. of the evaporation-residue had risen from 161 to 191, yet the value was not high enough to warrant the conclusion that the oil had been adulterated. The authors further point out that in order to determine the evaporation-residue it is not enough to heat the oil on the water-bath for two hours only, as is said to be done occasionally. In one experiment constancy of weight was only reached after 9½ hours with 5,82 p.c. residue, while the evaporation-residue after 3 hours' heating was 6,61 p.c.

We may add to the above that the second of the two methods referred to is useless for the special estimation of glyceryl esters, if for no other reason, because other sparingly volatilisable esters, such as triethyl citrate, would be left behind in the evaporation-residue; hence the method could only give a general indication for sparingly-volatile esters. With regard to the method devised by ourselves, we have shown in

¹) Perfum. and Essent. Oil Record 3 (1912), 275. ²) Salamon and Seaber do not state who is the author of this method.
our Report of October 1910 (61) that it is capable of detecting the presence of even 1 p. c. glyceryl acetate in bergamot oil, and that, if carried out according to the instructions given, an addition of 1 p. c. glyceryl acetate increases the quantity of KOH used up by about 15 milligrams (= 0.54 cc. seminormal potash liquor). In the case of two samples of bergamot oil to each of which 2 p. c. glyceryl acetate had been added, Salamon and Seaber used up respectively 1.3 and 1.8 cc. seminormal potash liquor in order to saponify the alcoholic solution, which would represent about 2 to 3 p. c. glyceryl esters. These values approximate very closely to the facts.

S. Godfrey Hall and A. J. Harvey 1) have recently published another method for the quantitative estimation of glyceryl esters in bergamot and lavender oils. Put briefly, this method is based upon the direct separation and estimation of the glycerol. The authors proceed as follows:

A known quantity of oil (not less than 10 grams if possible) is mixed with 50 cc. alcohol, (sp. gr. 0.830) and saponified with seminormal potash-liquor. After being digested for one hour on the water-bath the solution is neutralised with seminormal hydrochloric acid, evaporated to dryness on the water-bath, and the residue diluted with about 20 cc. water and extracted with methylalcoholic ether to remove the oily portions. The ether-solution is again shaken out with 10 cc. water, added to the aqueous extract, and the whole evaporated to a syrupy consistency. If the original oil was adulterated with glyceryl ester, the remaining residue must contain the corresponding glycerol, of which the quantity is estimated by acetylation. In order to accomplish this the residue is diluted with 3 grams fused sodium acetate and 8 cc. acetic anhydride and heated for one hour in a reflux-condenser. It is then cooled, 50 cc. boiling water is added, the whole brought to a temperature of 80°, again cooled, and finally filtered quantitatively into another vessel, by rinsing with water. After adding a few drops of phenolphthalein solution the excess of acetic acid is neutralised lege artis with a 5 to 6 p. c. soda liquor and the mixture saponified with seminormal soda liquor, being boiled gently for 15 minutes in a reflux condenser. After cooling the excess of liquor is titrated back with seminormal hydrochloric acid and the quantity of glycerol or glyceryl acetate calculated from the alkali used up (1 cc. seminormal soda liquor corresponds to 0.01535 grams glycerol and 0.03641 grams glyceryl acetate). It is advisable to make a blank test at the same time, and for this 5 cc. of the seminormal liquor is used. Hall and Harvey have tested their method with bergamot and lavender oils, to which they had added 2 and 5 p. c. glyceryl acetate respectively and have obtained excellent results, as is shown in a table added to their paper.

As mentioned in another part of the present Report (p. 62), F. D. Dodge utilises the stability of eucalyptol towards 5 to 6 p. c. potassium permanganate solution in the cold for the purpose of the quantitative estimation of eucalyptol in oils of eucalyptus and cajuput. He has now experimented with this method in order to ascertain its value for other essential oils, and, has reported the results of his investigations to the Eighth International Congress of Applied Chemistry, which assembled in New York in September 1912 2).

According to Dodge's experience the process, when applied in the cold, usually takes a quantitative course. Among the more common constituents of essential oils only the following remain unattacked, viz., camphor, fenchone, bornyl acetate, menthyl

acetate, eucalyptol, paraffins, aliphatic ketones, and a few aromatic ketones. Borneol and fenchyl alcohol are oxidised into stable ketones. Among the hydrocarbons, cymene is rather refractory, but with the terpenes oxidation takes place very readily; in the case of camphene alone it proceeds somewhat more slowly. Among the oils which were tested the following were completely or almost completely oxidised by the process: oils of lemon, orange, turpentine, Java citronella (1 p.c. residue), lemongrass, linaloe, coriander, petitgrain, caraway, bitter almonds, cassia, wintergreen, bay, pimento, clove, cinnamon leaf and nutmeg. Other oils, according to their constitution, left a more or less considerable residue, for instance: oil of juniper berries left 4 p.c., sassafras 5 p.c. (including camphor), lavender 5 to 10 p.c., cardamom 8 p.c. (chiefly eucalyptol), cumin 20 p.c. (cymene), rosemary 35 p.c. (camphor, bornylacetate), spike 41 p.c. (eucalyptol, camphor), Siberian pine needle oil 60 p.c. (chiefly bornyl acetate) and oil of rue 90 p.c. (methylmonyl- and methylheptyl ketone).

According to Dodge, the potassium permanganate method is useful for detecting the presence of petroleum in turpentine oil and in citronella oil, as well as for the estimation of cineol.

For 10 cc. turpentine oil (which, as stated above, is completely oxidised), Dodge uses from 800 to 850 cc. potassium permanganate solution.

In the case of Ceylon citronella oil, it may happen that the non-oxidised portion contains a little camphor, generated from the borneol which is present in the oil, as a result of the permanganate treatment. This camphor can be removed with cold 80 p.c. sulphuric acid. Any residual petroleum may be detected by the fact that at 0° it does not mix with castor oil.

Dodge also recommends the method for distinguishing (and possibly for quantitatively estimating) bornyl acetate from the isomeric linalyl, geranyl and terpinyl acetates; bornyl acetate alone being stable. By subtraction from the total esters, which are determined by quantitative saponification, that portion of the esters which has been attacked by the potassium permanganate is estimated. By this method, Dodge found a Siberian pine-needle oil with 45,8 p.c. total esters to contain 38,3 p.c. bornyl acetate and 7,5 p.c. oxidisable esters (terpinyl acetate?), while a rosemary oil with 5,78 p.c. total esters contained 1,33 p.c. bornyl acetate and 4,45 p.c. of other esters.

We may here point out that the method of separating sparingly oxidisable bodies from others which are more readily oxidisable, by shaking with potassium permanganate solution, has long been known. We ourselves have frequently used it successfully in our investigations. Compare, for instance, Schimmel's Bericht April 1897, 50; Report April 1902, 24; April 1903, 25, 74; October 1912, 79.

Physical Notes.

L. Gurwitsch1) has made comparative experiments in the fractional distillation of oil-mixtures, both with and without steam, and has confirmed the theoretical conclusion that the passing-through of steam favourably affects fractionation. The author took care to work as far as possible under the same conditions and with the same apparatus. In order to obviate any possible dephlegmation he placed the entire still, together with its delivery tubes, in an oil-bath. For each experiment he took 1 litre of liquid-mixture, of which about 100 cc. was driven off. He used carefully purified Russian "Meteor" burning oil in his experiments. In lieu of introducing steam from without

1) Zeitschr. f. angew. Chem. 25, 1. (1913), 102.
the required water was placed within the still itself. The distillates obtained were fractionated with a Glinsky apparatus. The results were as follow:

<table>
<thead>
<tr>
<th>Distillation with water:</th>
<th>Fractionation of the distillate:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil driven off</td>
<td>B. p. 105 to 125°</td>
</tr>
<tr>
<td>104,0 cc.</td>
<td>125 to 140°</td>
</tr>
<tr>
<td>105,8 &quot;</td>
<td>22,0 p. c.</td>
</tr>
<tr>
<td></td>
<td>25,6 p. c.</td>
</tr>
<tr>
<td></td>
<td>22,5 &quot;</td>
</tr>
<tr>
<td></td>
<td>23,8 &quot;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distillation without water:</th>
<th>Fractionation of the distillate:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil driven off</td>
<td>B. p. 108 to 125°</td>
</tr>
<tr>
<td>103,4 cc.</td>
<td>125 to 140°</td>
</tr>
<tr>
<td>103,5 &quot;</td>
<td>15,8 p. c.</td>
</tr>
<tr>
<td></td>
<td>19,8 p. c.</td>
</tr>
<tr>
<td></td>
<td>17,1 &quot;</td>
</tr>
<tr>
<td></td>
<td>20,3 &quot;</td>
</tr>
</tbody>
</table>

It would appear to us that the theoretical foundation, namely the generalisation of Margules' formula, does not appear to be quite correct, but we do not desire to make further observations on the matter in this place, because it is our intention, when an opportunity offers, to deal experimentally with the subject in question.

On p. 133 of our last October Report we discussed a method which has been worked out by E. Deussen for testing the purity of optically active substances. In a second communication on the same subject, Deussen1) publishes further experimental results. Of particular importance in his method is the accurate determination of the optical rotation, as an error of even a hundredth part of a degree very considerably affects the value of the specific rotation, hence it is necessary to read off 8 or 10 times. Shortly after the publication of Deussen's second article, L. Tchugaeff2) published certain notes on Deussen's work. Tchugaeff has ascertained that Deussen in his careful investigation of the literature on the subject has overlooked precisely the work of those authors3) who since the year 1896 have been engaged in the study of the conditions of rotation of coloured compounds and of compounds showing abnormal rotatory dispersion generally. Tchugaeff further specially points out that about 18 months ago4) he himself proposed a method by which it is possible to utilise the rotatory dispersion for the analysis of optically active mixtures to a far wider extent than can be done by Deussen's method. In conclusion, Tchugaeff points out that the monochromatic mercury light used by Deussen cannot have a wave-length of 491 μm, as stated by Deussen, but of 546 μm. Herein Deussen5) agrees with Tchugaeff, but he also observes that in his experiments he made use of a solution of potassium bichromate, Guinea-green-B-extra and aesculin, which, according to a reference in the book by Plotnikoff (Photochem. Versuchstechnik, Leipzig 1912, p. 20) ought to give a light of 491,6 μm wave-length, but which actually probably only allows of the penetration of a light of 546 μm. Deussen nevertheless remains convinced that in the testing of the purity of optically active bodies he has gone a step in advance of Tchugaeff, since he has pointed out how it is possible to recognise the absolute purity of an optically active substance.

Finally there remains to be mentioned a rejoinder by Plotnikoff6) to Deussen's statement. Plotnikoff points out that any colouring material, given a sufficiently weak

concentration, is able to allow all lines to pass, but that if the concentration is suitably chosen only a few, in many cases only a single, line passes.

As already previously mentioned, von Auwers and Roth¹) have successfully made use of the estimation of the thermic value in the determination of the constitution of alicyclic compounds. Roth has now continued his researches in collaboration with G. J. Östling⁵) and has found that Stohmann's law of the correspondence of caloric value and dissociation-constants applies admirably in the case of the simple polymethyleneic acids.

Generally speaking, the serial sequence of the energy-content is as follows: pentacyclic ring, hexacyclic ring, double-bond, tricyclic ring, quadricyclic ring. Apparently a heptacyclic ring possesses a somewhat higher energy-content than does a hexacyclic ring. So far as can be judged from the solitary compound which has been examined, the spirocyclic arrangement of the carbon-atoms appears to be fairly stable.

Roth and Östling have determined the thermochemical behaviour of the following bodies which are of special interest to us: α-tanacetone dimethylcarboxylate, α-tanacetone ketocarboxylic acid, cis-methyl norpinate, dimethyl pinate, methyl pinonate, cyclofenchene, thujane, thuylalcohol, thujone, and camphor.

From the experimental results obtained by other authors, especially Vanstone⁴), Jouniaux⁴), using the familiar thermodynamic formulæ, has calculated the following constants of camphor.

Degree of heat at melting . . . . . . . . . . 8,23 cal.
    " " " " evaporation . . . . . . . . . . 93,17 "
Density of steam . . . . . . . . . . . . . . normal
Ebullioscopic constant . . . . . . . . . . . . 50,2

The values obtained by the different formulæ are in satisfactory agreement. The values given by Ramsay and Young were deliberately omitted.

**Pharmaco-physiological Notes.**

We may here refer to a paper by J. R. Rippetoe and L. E. Wise⁵) on the conserving action of essential oils. The authors investigated the development of mould-fungus in solutions of glucose and of sugar-peptone in the presence of essential oils of the most different descriptions. Among others, bitter almond oil, cajuput oil, citronella oil, clove oil, eucalyptus oil and peppermint oil had a conserving action. Oils of angelica, lemon sandal wood and turpentine, among others, were inactive, while with oils of Russian anise, caraway, ginger, lemongrass, and a few others the effect was doubtful.

H. Schwalb, in a thesis on comparative investigations in the pharmacology of the terpene-series (Göttingen 1912)⁶), describes a series of experiments made by him with various terpene-bodies upon the hearts of frogs and upon paramecæia⁷). Schwalb found

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that the vapours of \( p \)-cymene, \( \alpha \)-terpinene, \( \Delta^2 \)-menthene and menthane in a concentration of 0.004 to 0.013 gram per liter of air cause paralysis of the isolated heart of the frog, after a more or less clearly-defined stage of excitement. Carvone, dihydrocarvone, tetrahydrocarvone, menthol, menthene, \( \Delta^1 \)-menthene-3, camphor, and borneol, given in a concentration of 1:40000 in physiological solution of salt, lowered the function of the isolated heart of the frog immediately after they began to affect the ventricles. When, after a short time, the solution of the products above-named was removed and replaced by a fresh solution of salt, a brief augmentation of the heart-function, exceeding the normal, generally ensued. Menthol appears to form an exception to this rule. Even after the menthol-solution was removed and the heart washed-out with a pure solution of salt it remained affected to a certain degree. With regard to the experiments with paramæcia, the ketones cause a condition of excitement of which the duration depends upon the degree of concentration; this is followed by paralysis. Noteworthy variations in the degree of activity were observed within the groups menthone-menthenone and carvone-dihydrocarvone-tetrahydrocarvone. These variations run parallel with similar variations in the lowering of the surface-tension in aqueous solutions.

It appears from an investigation by O. Loeb\(^1\) that the internal and subcutaneous administration of aliphatic aldehydes (such as formaldehyde, formaldehyde-sodium bisulphite, acetaldehyde, paraldehyde, isobutylaldehyde, valeraldehyde, oenanthic aldehyde and citral) to rabbits produces symptoms of arterio-necrosis. Furfurol, aromatic aldehydes (benzaldehyde, salicylic aldehyde, and cinnamic aldehyde), ketones (acetone and diethyl ketone), and alcohols (methyl and ethyl alcohol) have no such effect.

On the irritant action of pastinac upon the skin, see p. 78.

On the pharmacological action of sandalwood oil see p. 94.

**Phyto-physiological Notes.**

When testing the suitability for pharmaceutical purposes of valerian root grown in the neighbourhood of Würzburg, W. Unger\(^2\) discovered that the essential oil contained in the corky hypodermic cells of valerian root is surrounded by an exceedingly tender envelope, which becomes perceptible only after the oil has been removed. Pressed to the wall of the envelope a minute body, usually shattered into fragments, is frequently discovered. This body may be the remains of a previous cellular nucleus. The envelope may be seen in a much finer form in the large oil-drops which sometimes occur in the layers of the cells of the bark adjoining the hypodermis. When these oil-drops are dissolved a circular ring becomes perceptible. It is difficult to give an opinion on the chemical character of the envelope, but it is certain that it consists neither of protoplasm nor of the residue of an undissolved secretion. Its extraordinary thinness is a great obstacle to the application of colour-tests. Apparently the envelope is wholly indifferent towards potash liquor and copper oxide ammonia.

Unger states that in other plants also the oil-drops may be contained within an envelope. Sections of cherry laurel leaves afford instructive instances of this fact.

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\(^1\) *Arch. f. exp. Pathol. u. Pharmak.* 69 (1912), 114; *Chem. Zentralbl.* 1912, II, 1142. — \(^2\) *Apotheker Ztg.* 27 (1912), 1021.
Trabut\(^1\) has noticed a peculiar property of cultivated *Citrus*-species. He has observed that specimens which at first throve well, became etiolated in the second year. Curiously enough, the disease may be communicated by grafting. A diseased wild plant will infect a healthy scion, and conversely a healthy wild tree is infected by being grafted with a diseased scion. So far nothing is known of the origin of the disease. Baur\(^2\) has observed a similar peculiarity in the *Malvaceae*.

On the distribution of emulsin-like enzymes see p. 21.

On the distribution of primverin, primulaverin and primverase in the Vegetable Kingdom, see p. 84.

**Chemical Notes.**

It will be remembered that some time ago we referred to a method for the determination of a standard for the unsaturated character of hydroaromatic compounds which has been worked out by J. Klimont and W. Neumann\(^3\).

The first-named author\(^4\) has now published details on the method of carrying out this determination.

W. Ipatieff\(^5\) has already on previous occasions published papers on the influence of subsidiary substances on the activity of catalysers. Thus, for example, the catalytic properties of copper oxide or of reduced copper are considerably impaired when hydrogenation takes place in a phosphorbronze instead of in an iron pipe. By using simultaneously catalysers of different action, Ipatieff\(^6\) has obtained interesting results. For example, camphor, in the presence of nickel oxide and hydrogen under high pressure at 320 to 350\(^\circ\)C, is converted in borneol. In order to reconvert borneol into camphor, the former body must be heated with aluminium oxide under high pressure at 350 to 360\(^\circ\). Quite different results were obtained by acting with hydrogen in the presence of both catalysers. 30 grams \(d\)-camphor were heated at 200\(^\circ\) with 3 grams nickel oxide and 1.5 grams aluminium oxide for 24 hours in a hydrogen-atmosphere under pressure. The reaction-product consisted of \(isocamphane\) (m. p. 64 to 64.5\(^\circ\); b. p. 164 to 165\(^\circ\)). Carvomenthone afforded pure menthane. \(d\)-Borneol, by the same method, also afforded \(isocamphane\). When \(isoborneol\) was heated at 350 to 360\(^\circ\) with aluminium oxide only it yielded crystalline camphene, but the joint reaction of nickel and aluminium oxide led to \(isocamphane\). An altogether different result is obtained when, instead of nickel and aluminium oxide, a mixture of the latter and copper oxide is employed. In that case borneol affords a mixture of solid and liquid camphene. The solid camphene may possibly be contaminated with bornylene.

Hydrogenation for 24 hours of \(d\)-fenchone in the presence of nickel oxide under pressure at 240\(^\circ\) yields fenchol (b. p. 196\(^\circ\); \(d_200\) 0.9594; \(\alpha_D + 0\)) which can only with difficulty be converted into fenchene when aluminium oxide alone is used. The reaction again takes a different course in the presence of nickel oxide and aluminium oxide. Reduction then takes place at as low a temperature as 215\(^\circ\), and is completed within 12 to 14 hours, fenchane, b. p. 162 to 163\(^\circ\); \(d_{170} 0.8766\), being formed.

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Ipatieff\(^1\)) also mentions an improvement in his method of hydrogenation which consists in the introduction in his apparatus of an arrangement (designed by W. Werchoffsky) or stirring under high pressures. This arrangement is on the solenoid-principle; experiments for its simplification are still in progress. With the aid of this arrangement Ipatieff was able to reduce a series of bodies which are otherwise difficult to hydrogenate. Among these, using palladium as a catalyst, he obtained from geraniol a satisfactory yield of a decanol, b.p. 105 to 106° (15 mm.); \(d_{180}^{\text{o}} 0,8280\). Citral also readily afforded a decanol, b.p. 107 to 108° (12 mm.); \(d_{180}^{\text{o}} 0,8296\).

As the simplest method of hydrogenating unsaturated bodies in a colloid platinum metal solution, A. Skita and W. A. Meyer\(^2\) recommend the addition to the solution of platinum chloride and gum arabic of a colloid palladium or platinum solution. In that case, as soon as the hydrogen is forced in, a colloid platinum solution is formed, suited for transferring the hydrogen to the material which is to be reduced. In the reduction of unsaturated ketones and aldehydes the addition of colloid platinum metals is superfluous, because where these bodies are present when the hydrogen is introduced a colloid platinum metal solution is immediately formed. But in the reduction of bodies which are neither aldehydes nor ketones the platinum metal is precipitated in granular form, under the action of hydrogen. Although palladium is capable, even in this form, of attaching hydrogen to certain aromatic unsaturated groups, the method fails when it is tried to attach aromatic double-bonds, that is to say in the case of benzene, naphthalene, &c. For example, it was possible to reduce \(\tau\)-camphene in the presence of palladium chloride and gum arabic in alcoholic solution, the palladium being precipitated in the metallic form. Within about one hour the theoretical quantity of hydrogen had been absorbed, dihydrocamphene (m.p. 53°; b.p. 161 to 162°), being formed.

The authors also describe the reduction of pinene from American oil of turpentine (b.p. 155 to 160°) in alcoholic solution in the presence of a colloid palladium hydroprotoxide solution. In this case pinane, b.p. 164 to 166°, resulted.

We may in conclusion refer to the hydrogenation of cinnamic acid. To accomplish this 7,4 grams cinnamic acid in dilute alcoholic solution was diluted with 0,2 grams platinum-hydrochloric acid, 0,2 grams gum arabic and a colloid platinum solution (0,0005 grams platinum) and shaken with hydrogen under 1 atm. over-pressure. The double-bond was reduced within 15 minutes.

Elsewhere\(^3\) Skita and Meyer describe the hydrogenation of \(\alpha\)-camphene (heptylic aldehyde) into heptylalcohol.

**Hydrocarbons.**

Pulegene. Wallach\(^4\) has discovered that it is impossible to reduce pulegene sufficiently by Paal's method but that it can be so reduced by Skita's method. For this purpose the hydrocarbon was emulsified in 5 p.c. acetic acid, diluted with palladium chloride and gum arabic and shaken for three days in a hydrogen atmosphere. Dihydro-pulegene (methyl-1-isopropyl-3-cyclopentane) boils between 142 and 144°, \(d_{190}^{\text{o}} 0,7730\).

Camphene. As stated in our *Report* of April 1912, p. 169, von Auwers, as a result of spectrochemical investigation, has convinced himself of the accuracy of Wagner's

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camphene formula (I). W. N. Haworth and A. T. King\(^1\) have now tried to ascertain the constitution of camphene chemically, by the synthesis of camphenic acid and its products of resolution. Aschan\(^2\) some time ago obtained dehydrocamphenic acid by treating monobromocamphenic acid with alkali. With nitric acid this dehydrocamphenic acid can be oxidised into a lactone, which Aschan regards as the lactone of \(\alpha,\alpha\)-dimethyl-\(\beta\)-hydroxy-adipic-\(\beta\)-carboxylic acid. Haworth and King have endeavoured to synthetise this lactone. They started from ethyl \(\alpha\)-ketoglutarate (II), which they condensed with ethyl \(\alpha\)-bromoisobutyrate (III), whereby ethyl \(\beta\)-hydroxy-\(\alpha\)-dimethylbutane-\(\alpha,\beta,\delta\)-tricarboxylate (IV) was generated.

\[
\begin{align*}
\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{C}_2\text{H}_5 &+ \text{C(CH}_3)_2\text{Br}\cdot\text{CO}_2\text{C}_2\text{H}_5 \quad \text{II.} \\
\text{CO}_2\text{C}_3\text{H}_5 &+ \text{CH}_2\cdot\text{C}(\text{OH})\text{C}(\text{CH}_3)_2\cdot\text{CO}_2\text{C}_2\text{H}_5 \quad \text{III.} \\
\text{CH}_2\cdot\text{CO}_2\text{C}_2\text{H}_5 &+ \text{CH}_2\cdot\text{CO}_2\text{C}_2\text{H}_5 \quad \text{IV.}
\end{align*}
\]

This ester they hydrolysed with 15 p.c. hydrochloric acid. The free lactonic acid, \(\text{C}_9\text{H}_{15}\text{O}_6\), melts at 159\(^\circ\); when heated to about 165\(^\circ\) it is converted into its anhydride, m. p. 104\(^\circ\). It is not identical with the lactonic acid m. p. 256\(^\circ\) which was obtained by Aschan as the degradation product of camphenic acid; hence the formula assigned to his acid by Aschan is untenable.

On the reduction of camphene, see p. 134.

**Pinene.** It will be remembered that some time ago G. G. Henderson and M. M. J. Sutherland\(^3\) oxidised camphene with hydrogen peroxide. They have recently also treated pinene with this oxidising agent\(^4\) and have obtained as reaction-products compounds which can be no longer derived from the pinene-ring. The pinene was separated from American turpentine oil by repeated fractional steam distillation (b. p. 155 to 156\(^\circ\)\(^5\)) and was oxidised in a solution of glacial acetic acid with 30 p.c. aqueous solution of hydrogen peroxide at 40 to 60\(^\circ\). From the neutral reaction-products the authors obtained with bisulphite an aldehyde \(\text{C}_{10}\text{H}_{16}\text{O}\) (semicarbazone, m. p. 190 to 191\(^\circ\), which proved to be exactly similar to the body of the same structure\(^6\)) obtained from pinene by oxidation with chromyl chloride. After removal of the aldehyde the authors isolated from the reaction-mass free \(\alpha\)-terpineol (m. p. 35\(^\circ\); phenylurethane, m. p. 113\(^\circ\)) and terpinyl acetate, as well as bornyl acetate (borneol, m. p. 203\(^\circ\)), dipentene (tetra-bromide, m. p. 125\(^\circ\)), and a body \(\text{C}_{10}\text{H}_{16}\text{O}_3\), m. p. 95 to 96\(^\circ\), which was not volatilisable with steam, and which is most probably menthane-1, 4, 8-triol (trihydroxyterpane). Trihydroxyterpane was already known as an oxidation product of \(\Delta^{(10)}\)-menthenol-1 (\(\gamma\)-terpineol)\(^7\), but so far it does not appear to have been observed as a derivative of pinene.

No glycol or ketone, such as is afforded by camphene upon oxidation with hydrogen peroxide was yielded by pinene.

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The preparation of pinene hydriodide by Wagner and Brickners's method is troublesome, and yields poor results, especially in cases where the hydriodic acid cannot be dried completely. According to O. Aschan, pinene hydriodide can be prepared much more easily by allowing anhydrous magnesium iodide to react upon pinene hydrochloride. On 10 parts powdered magnesium Aschan pours 150 parts absolute ether, the mixture being diluted under steady cooling with 100 parts iodine. When the reaction is completed 136 parts pure pinene hydrochloride are introduced, the mixture being heated for two hours in a reflux condenser. The ether is then distilled off and the residue heated for three hours more in a water-bath. Small pieces of ice are added to the solid residue, the resulting oil is decolorised with bisulphite and driven over with steam. A colourless oil then distils over, which is heated in a water bath with 400 parts 15 p. c. alcoholic potash liquor and subjected to steam-distillation. In this manipulation a light oil, consisting of camphane and a little bornylene, distills over first, and afterwards a heavy oil which sinks to the bottom and of which the major portion boils between 99 and 100° (6 mm.) (d^30_40 1.4553). The latter substance is pinene hydrochloride. Pinene hydriodide from faintly rotating or inactive pinene hydrochloride melts at about —12°; pinene hydriodide from strongly rotating crude material at —3 to —5°.

When treated with freshly-precipitated silver oxide in alcoholic solution, pinene hydriodide yields what is apparently a new terpene alcohol, C_{10}H_{17}.OH, which is unsaturated, as is evident from its behaviour towards permanganate and bromine. B. p. 207 to 211°.

The preparation of camphane from pinene hydriodide, which was formerly carried out by Aschan with glacial acetic-hydriodic acid can just as readily be accomplished with hydrogen chloride-glacial acetic acid. In this case the iodide is diluted in the presence of zinc-wool, under steady cooling, with 12 p. c. hydrogen chloride-glacial acetic acid, the mixture being finally boiled for a few hours in a reflux condenser. J. Hämäläinen has recently succeeded in converting the camphane into camphor derivatives, a fact which is of importance because it proves beyond doubt that camphane forms the basic hydrocarbon of the camphor-compounds.

On the reduction of pinene, see p. 134.

Menthadiene. In our Report of April 1912 (p. 173), we mentioned that G. G. Henderson and R. Boyd had obtained a menthiadiene from thymol, from primarily-produced thymomenthol and Δ^4-menthene. Henderson, in collaboration with S. P. Schotz, has now prepared a menthiadiene from carvacrol by the same method. He hydrogenated carvacrol in the presence of finely-divided nickel to carvomenthol and converted the latter into a menthene (most probably Δ^1-menthene), by heating with anhydrous oxalic acid. The dibromide of the menthene (1,2-dibromomenthane) when heated with anhydrous sodium acetate in glacial acetic acid solution, or when boiled with alcoholic potash liquor, yielded a menthiadiene, b. p. 172 to 174°: d^20_40 0.8272, n_p 1.46430. So far it is impossible to give definite data with regard to the constitution of this menthiadiene, but it is certain that the menthiadiene of Henderson and Schotz differs from that which has been prepared from carvomenthol chloride by Kondakow and Schindelmeiser. The former affords no nitrite, whereas Kondakow's menthiadiene yields a "nitrosite", and is

probably identical with \( \beta \)-phellandrene (\( \Delta^{137} \)-menthadiene). The authors believe that intramolecular rearrangements have occurred during the formation of the \( \Delta^{1} \)-menthene dibromide, or during the process of the splitting-off of bromine from that dibromide. Theoretically the formation of \( \alpha \)- or \( \beta \)-phellandrene is to be expected.

Sesquiterpene (?) from \( \alpha \)-hederagenin. From \( \alpha \)-hederin, a glucoside found in ivy-leaves, and insoluble in water, A. W. van der Haar\(^1\)) has obtained, by hydrolysis with dilute sulphuric acid, arabinose and a methyl-pentose as well as \( \alpha \)-hederagenin. Upon distillation in a current of hydrogen, \( \alpha \)-hederagenin yields an oil which volatilises with steam; b. p. 245 to 255°, \( n_{D}^{20} \) 1,5303. Determination of the molecular weight and combustion showed the substance to possess the composition of a sesquiterpene \( \text{C}_{15}\text{H}_{24} \).

Selinene. In our Report of April 1910, p. 32, we described the isolation of a sesquiterpene from celery oil, to which we gave the name of selinene and from which we obtained a dihydrochloride from which it was possible to recover the sesquiterpene. Afterwards F. W. Semmler and F. Risse\(^2\) took up the study of selinene and discovered that in the preparation of selinene dihydrochloride it is of advantage to pass into the essential solution of the sesquiterpene a mixture of one part hydrochloric acid gas and three parts of air, better yields being obtained by this method than from the introduction of pure hydrochloric acid gas. The authors did not regenerate the selinene from the dihydrochloride with sodium ethylate, as we did, but with saturated methyl alcoholic potash liquor. They first allowed the hydrochloride to stand for a few hours with this liquor at room-temperature, after which they gradually raised the temperature, finally heating the mixture on the water-bath. By this method they obtained a sesquiterpene with the following constants: b. p. 128 to 132° (11 mm.), \( d_{20}^{0} \) 0,9190, \( \alpha_{D} + 61°36' \), \( n_{D} \) 1,50920. These values are in agreement with the constants of the sesquiterpene which was obtained by us, but the rotation is higher. Hence Semmler and Risse are of opinion that it is not impossible that in our case the rotation was depressed through the presence of a second sesquiterpene and that, on the other hand, the mild reagent used by them did not perceptibly change the hydrocarbon. When selinene dihydrochloride is reduced with sodium and alcohol it yields tetrahydroselinene. A simpler method of arriving at the same hydrocarbon is to reduce selinene with platinum and hydrogen. The tetrahydroselinene obtained by this method boils at 126 to 128° (10,5 mm.): \( d_{20}^{0} \) 0,8881, \( \alpha_{D} + 7° \), \( n_{D} \) 1,48259. By treating selinene dihydrochloride with milk of lime the authors obtained a bicyclic, simply unsaturated alcohol \( \text{C}_{15}\text{H}_{26}\text{O} \) which they call selinenol: b. p. 155 to 163° (19 mm.), \( d_{20}^{0} \) 0,9627, \( \alpha_{D} + 52°36' \), \( n_{D} \) 1,50895. In addition there were formed selinene and, apparently, a glycol \( \text{C}_{15}\text{H}_{25}\text{O}_{3} \). When reduced with platinum and hydrogen selinenol is converted into dihydroselinenol, m. p. 86 to 87°. The authors recommend the preparation of dihydroselinenol for the purpose of detecting the presence of selinene.

Semmler and Risse\(^3\) also describe the products obtained by them in oxidising selinene with ozone. From natural selinene they obtained as a neutral oxidation-product a diketone \( \text{C}_{15}\text{H}_{20}\text{O}_{4} \) which, when separated from the disemicarbazone (m. p. 228°), boils between 178 and 180° (11 mm.): \( d_{20}^{0} \) 1,0566, \( \alpha_{D} + 15° \), \( n_{D} \) 1,4994. When the formula of the diketone is compared with that of selinene it is clear that two carbon atoms must have been split off which are attached to the residual carbon nucleus, \( \text{C}_{15} \), either in a side-chain or semicyclically. Furthermore, the diketone being completely

saturated, two rings must exist both in it and also in selinene. But in the process of oxidising with alkaline bromine solution an acid is formed which contains only one carbon atom less, from which fact Semmler and Risse conclude that the two keto-groups can only exist in one single form, that is to say, once as a methyl keto-group and the second time as a keto-group in ring-formation. From this they again conclude that the structure of natural selinene can only be of such a character that at one time a methylene-group occurs in a side-chain, while the second time a methylene-group is directly bound to the ring. Hence, natural selinene would belong to the class of pseudo-sesquiterpenes (semicyclic sesquiterpenes). When natural selinene (ortho-selinene) is ozonised, there is formed a small proportion of an acid product which has been shown to be identical with the acid from regenerated selinene described below.

The latter body yielded, as a neutral ozonisation-product, the diketone described above (semicarbazone, m. p. 228°) and, as an acid oxidation-product, an acid: selinene-diketo monocarboxylic acid, C_{14}H_{22}O_{4}, of which the methylester boils between 185 and 190° (11 mm.): d_{20} 1.0635, \( \alpha_d +4.24' \), \( n_d 1.47889 \). As only an exceedingly minute proportion of diketone had been formed, the authors assume that in the process of regeneration the semicyclic selinene is generated only in a minor degree. The formation of a diketomonocarboxylic acid appears to indicate that during the elimination of hydrogen chloride the double bond has been transposed into the ring. The following formulæ are given in order to make the separate reactions more intelligible:

The natural selinene is therefore a mixture, which consists principally of semicyclic pseudo-(\( \beta \))-selinene, and contains but little ortho-(\( \alpha \))-selinene.
The diketone \( C_{14}H_{22}O_4 \) from natural selinene referred to above has been further oxidised with alkaline bromine solution by Semmler and Risse\(^1\), who obtained from it a tricarboxylic acid \( C_{12}H_{15}O_6 \), m.p. 188°, of which the methylester \( C_{15}H_{24}O_5 \) boils between 200 and 205° (8 mm.). The acid being tribasic, it follows that the diketone must contain in the first place a \( COOH \)- and secondly a \( CO \)-group in a ring which undergoes disruption during oxidation, by which both the keto-group and the \( CH_2 \)-group adjacent to the keto-group are oxidised into carboxylic groups.

Diketomonocarboxylic acid \( C_{14}H_{22}O_4 \) from the regenerated selinene (see above), when oxidised with alkaline bromine-solution yields the same ketomonocarboxylic acid, m.p. 188°.

**Cymene.** P. Sabatier and E. Senderens\(^5\) have obtained \( \alpha \), \( m \), and \( p \)-menthane from \( \alpha \), \( m \), and \( p \)-cymene by passing the vapours, mixed with hydrogen, over heated nickel. \( m \)-Menthan has also been prepared by the reduction of \( d \)-sylvestrene, and this preparation showed a greater density \( (d^{10}_{20} 0,8116; [\alpha]_b +1,60^\circ) \) than did the inactive product from \( m \)-cymene \( (d^{10}_{20} 0,7965) \).

**Alcohols.**

Menthol. H. Rupe\(^2\), in a paper on the effect of the constitution upon the rotation of optically active bodies, describes the menthylesters of numerous derivatives of acetylacetic and benzoylacetic acids, as well as of \( \alpha \)-benzylcinnamic and dibenzylacetic acids.

By warming menthol with phenylacetic acid in the presence of sulphuric acid J. B. Senderens and J. Aboulenc\(^4\) have obtained menthyl-phenylacetate, a colourless liquid, b.p. 205,5° (25 mm.), \( d_{170} 0,9887 \). The menthylester of phenylpropionic acid melts at 28,5° and boils at 216° (25 mm).

Cyclohexanol, when heated with benzoic acid or its homologues and sulphuric acid, does not afford the expected ester, but yields cyclohexene instead. But with phenylacetic or phenylpropionic acids, in which the acid group is not linked directly to the nucleus, esterification takes place readily.

Bornyle. When preparing camphene from borneol and dilute sulphuric acid, P. Golubeff\(^5\) obtained as a by-product bornyl ether, \( (C_{10}H_{15})_2O \), b.p. 312 to 314° \( (d^{10}_{20} 0,960; [\alpha]_b -88,56^\circ; n_{D} 1,494) \), which, when oxidised with nitric acid, affords camphor. Heated under pressure with hydrochloric acid, it yields camphene hydrochloride. The principal product formed in the reaction was a camphene which showed a great resemblance to the camphene of Siberian pine-needle oil, but which was inactive: m.p. 48 to 49°, b.p. 157 to 160°.

On a terpene alcohol from pinène hydriodide, see p. 136.

**Aldehydes.**

L. Wolff\(^9\) has worked out a method for substituting hydrogen for the oxygen-atom of the ketones and aldehydes. With this object in view he heats the semicarbazones

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or hydrazones of the aldehydes or ketones with an absolute solution of sodium ethylate. If the heating-temperature is not sufficiently high the semicarbazones afford the hydrazones as intermediary products, and at a higher temperature the latter are converted into the hydrocarbons. The reaction proceeds as follows:—

\[ C:N\cdot\text{NH} \cdot \text{CONH}_2 + \text{H}_2\text{O} = C:N\cdot\text{NH}_2 + \text{CO}_2 + \text{NH}_3 \]
\[ C:N\cdot\text{NH}_2 = \text{CH}_3 \cdot 2\text{N}. \]

The method is applicable to aliphatic and aromatic ketones; in fact, to cyclic ketones generally, as well as to ketoic acids. In the case of unsaturated aldehydes and ketones the reaction has this advantage over other reduction-methods that the double bonds are preserved, although the possibility of a displacement must be reckoned with.

Menthone hydrazone (b. p. 124° at 11 mm.) was obtained from the semicarbazone (m. p. 184°) by heating with soda liquor to 160°. It is, however, also obtainable by heating menthone for 6 hours with hydrazine hydrate to 160°. A 10 hours' heating of the hydrazone with sodium ethylate solution to 170° afforded hexahydrocymene (menthane). Camphor hydrazone (m. p. 55°: b. p. 119 to 120° at 13 mm.) yielded camphane, m. p. 156 to 157°; b. p. 161° (757 mm.). When exposed to air camphor hydrazone liquifies, giving rise to a hydrate, m. p. 44°.

d-Fenchone ([α]_D + 62,8°), when heated with hydrazine hydrate, was converted into d-hydrazone: m. p. 56 to 57°, b. p. 230 to 231°, [α]_D + 46,4° (11 p. c. alcoh. solution). When heated with sodium ethylate, the hydrazone yields l-fenchane, b. p. 149°: d_19^20 0,8316, [α]_D — 18,11° (1,058 grams fenchane in 20 cc. alcohol), n_D20 1,4462. It is a noteworthy fact that fenchane is laevorotatory, whereas the fenchone which has been employed and its hydrazone are dextrorotatory. In other cases also, Wolff has observed a reversal of the direction of rotation; e. g. in d-carvone, which is converted into a mixture of l-limonene and dipentene. It is therefore possible that the fenchane may not be optically uniform.

Vanillin semicarbazone or hydrazone yields with sodium ethylate, creosol (b. p. 221°).

Citronellal hydrazone when heated with sodium ethylate gives rise to a mixture of dimethyl octene and citronellol.

Citral. Continuing his experiments in the electrolytic reduction of aldehydes and ketones, H. D. Law¹) has ascertained that the presence of finely-divided copper accelerates reduction. When copper foil was used as a cathode the addition of copper sulphate to the cathode solution proved to be very useful, inasmuch as it causes the deposition, during electrolysis, of a precipitate of finely-divided, highly-active copper upon the cathodes. 50 grams of citral yielded the following quantities of substance volatilisable with steam, cathodes of various descriptions being employed:—

| Sheet lead cathode (10 mm.) | 7,5 g. |
| Sheet Copper " (0,7 mm.) | 10 g. |
| Copper Foil " (0,06 mm.) | 27 g. |
| Sheet lead " (0,06 mm.) + 1 g. Copper sulphate | 45 g. |

The volatile reduction-product was identical with the geraniol-mixture described in the author's previous communication²).

Pulegone (sheet lead being used as cathode) yielded from 50 to 60 p. c. menthone, as well as a heavy, plumbiferous, red oil. With copper electrodes from 95 to 100 p. c. menthone was obtained. Carvone, when reduced with copper-foil-cathodes and copper sulphate, was almost entirely converted into dihydrocarvone.

**Phenylacetalddehyde.** E. Späth\(^1\) reports on a \(\alpha\)-hydroxylactone of phenylacetalddehyde. He has observed that this aldehyde does not react with cyanide of potassium in the ordinary way, but that while condensing it unites with one molecule of hydrocyanic acid:

\[
2 \text{C}_8\text{H}_8\text{O} + \text{KCN} + \text{H}_2\text{O} = \text{C}_{17}\text{H}_{17}\text{O}_8\text{N} + \text{KOH}
\]

Saponification of the nitrile yields a lactone, \(\text{C}_{17}\text{H}_{19}\text{O}_9\), \(\alpha\)-hydroxy-\(\beta\)-phenyl-\(\gamma\)-benzyl butyrolactone, which E. Erlenmeyer jun. and F. Reis\(^2\) prepared several years ago by a different method. Hence the nitrile prepared from phenylacetalddehyde must be regarded as \(\alpha\),\(\gamma\)-diphenyl-\(\beta\)-hydroxybutyraldehyde cyanohydrine. \(\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CHOH}
\]

\[
\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH(OH)}\cdot\text{CN}
\]

On the arterio-necrotic action of certain aldehydes and ketones, see p. 132.

**Ketones.**

**Methylnonyl ketone.** E. Clemmensen\(^3\) has discovered that the reduction of aromatic ketones by heating them with amalgamated zinc and hydrochloric acid leads to the corresponding hydrocarbons. In the case of aliphatic ketones also the reaction takes place readily, albeit slowly. Thus, methylnonyl ketone from oil of rue afforded \(\text{n}\)-undecane, b.p. 193 to 195\(\circ\); \(d_{900}\) 0.741. Here the heating must be continued for 24 hours. In order to prepare the zinc amalgam, granulated zinc should be allowed to lie for about 2 hours in a 5 p. c. aqueous solution of corrosive sublimate.

**Methylheptenone.** It was formerly supposed that when water is split off from methylheptenone (I), — a reaction which takes place with ring formation —, dihydro-

\(m\)-xylene (II) is generated\(^4\). But, as Wallach\(^5\) has now discovered, the actual outcome of the reaction is a mixture of equal parts of xylene and tetrahydroxylene. It is impossible to prove this fact analytically, for the mixture gives values which agree for dihydroxylene. Wallach condensed methylheptenone by heating with zinc chloride or phosphorus pentoxide. The resulting mixture of hydrocarbons boiled principally between 130 and 140\(\circ\). When treated with dilute permanganate solution a hydrocarbon remained behind which was stable towards permanganate. This hydrocarbon, which constituted pretty nearly one-half of the original hydrocarbon mixture, proved to be \(m\)-xylene (III). The oxidation-liquors filtered off from the manganese dioxide, when extracted with chloroform yielded 1,3-dimethyl-3,4-dihydroxy\(c\)yclohexane (m. p. 89\(\circ\)) which when warmed with dilute sulphuric acid was converted into 1,3-dimethyl\(c\)yclohexanone. The ketone was identified by resolution into \(\beta\)-methyladipic acid, as well as by the preparation of its semicarbazone (m. p. 189\(\circ\)) and its oxime (m. p. 98 to 99\(\circ\)). The generation of dimethylidihydroxy\(c\)yclohexane from the condensation-products of

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methylheptenone is explainable only by the presence of tetrahydroxylene (IV) in the hydrocarbon mixture.

Wallach surmises that in the course of the auto-condensation of methylheptenone dihydroxylene is primarily formed, and that a portion of this body gives off two hydrogen-atoms, under formation of xylene, while another portion absorbs two atoms of hydrogen, giving rise to tetrahydroxylene.

Pinone, demethylated. In the course of the dry distillation of the calcium salt of cis-hexahydro isophthalic acid, O. Stark\(^1\) has obtained a ketone which he is inclined to consider as a demethylated pinone, of the formula given below. It boils between 157 and 158\(^{\circ}\) (758 mm.) and possesses an extremely pronounced, characteristic, somewhat camphoraceous odour. \(d_{20}^0\) 0.9322, \(n_{D20}^0\) 1.4731. Its semicarbazone melts between 179 and 180\(^{\circ}\).

Cyclic ketones. In our Report of October 1912 (p. 155) we referred to a paper by Wallach on the condensation-products of cyclic ketones with acetone, which had appeared in the Nachrichten der Königlichen Gesellschaft der Wiss. zu Göttingen, meeting of February 17\(^{th}\). Detailed particulars of Wallach’s investigations have now been published in another quarter\(^4\).

Menthone. J. Wanin\(^3\), while treating magnesium methyliodide with menthone, obtained methyl-3-menthanol-3: b. p. 102 to 103\(^{\circ}\) (16 mm.), \(d_{20}^{\text{petr}}\) 0.9143. The chloride boils at 101 to 103\(^{\circ}\) (13 mm.); and when heated with sodium bisulphate yields the hydrocarbon \(C_{11}H_{20}\), b. p. 185 to 187\(^{\circ}\), \(d_{20}^{\text{petr}}\) 0.8244.

Camphor. A few physical constants of camphor are quoted on p. 131.

Thujone. On p. 166 of our last Report we pointed out that pure thujane may be prepared from thujylidine hydrazine. Kishner\(^4\), while treating such a preparation with fuming hydrobromic acid, obtained bromides of which the stability depended on the duration of the reaction. After the elimination of hydrobromic acid the bromides afforded several hydrocarbons.

Menthenone. Some time ago A. Kötz and E. Anger\(^1\), in a brief communication, described an \(\alpha\)-menthone-5 (methyl-1-isopropyl-2-cyclohexanone-5), which they had prepared by reducing menthenone from Hagemann's ester. According to W. Dieckmann\(^2\), this menthone should be regarded as 3-methyl-2-isopropyl-cyclohexanone-1. Dieckmann assigns to the menthenone from Hagemann's ester the structure of \(\alpha\)-CH\(_2\) \(\alpha\)-3-methyl-2-isopropyl-cyclohexene-2-one-1, inasmuch as, when oxidised with potassium permanganate, it yields a satisfactory return of \(\gamma\)-acetobutyric acid and isobutyric acid.

Kötz and Anger state that the semicarbazone of the menthenone from Hagemann's ester melts at 152° or respectively at 138°, the oxime at 90 to 91°, but Dieckmann gives 167 to 168° and 104° respectively.

A reference to the electrolytic reduction of pulegone will be found on p. 141.

On the electrolytic reduction of carvone, see p. 141.

Ionone. A publication by A. Skita\(^3\) on hydrogenation with platinum-metals as catalysts contains some interesting data on the reduction of the ionones. \(\alpha\)-Ionone, in the presence of palladium chloride and gum arabic in dilute alcoholic solution, was shaken under over-pressure of 1 atm. until the quantity of hydrogen required for the reduction of a double bond had been absorbed. The reduction-product, dihydroionone, boiled between 121 and 122° (14 mm.); it had completely lost its characteristic aroma and only possessed a faint odour of cedarwood. By the same method, \(\beta\)-ionone yielded a dihydroionone with b. p. 126 to 129° (12 mm.). When the reduction is continued until hydrogen ceases to be absorbed, both \(\alpha\)- and \(\beta\)-ionone yield tetrahydroionone, b. p. 126 to 127° at 13 mm.

The fact that the reduction of \(\alpha\)- and \(\beta\)-ionone affords two different dihydroionones (I and II) indicates that the extracyclic bond is the first to be dissolved. This agrees with the fact that continued hydrogenation leads to the same tetrahydroionone (III).

\[\text{Dihydroionone from } \alpha\text{-ionone.}\]

\[\text{Dihydroionone from } \beta\text{-ionone.}\]

\[\text{III. Tetrahydroionone.}\]

---

Further proof of the last-mentioned assumption is seen by Skita in the fact that dihydro-ionone has, properly speaking, ceased to be an odoriferous body. Tiemann had already expressed the view that the odoriferous character of ionone was due to its $\alpha$, $\beta$-double bond. According to this view, a dihydro-ionone hydrogenated in its nucleus must be an odoriferous body. As a matter of fact, dihydrocyclodicitral and acetone, in the presence of tartaric acid, yield a dihydroionone, b.p. 124 to 125° (14 mm.) which possesses a pronounced odour reminding of ionone. Skita recommends that the name dihydro-ionone should be reserved for this body and that the two other dihydro-iones described above should be described respectively as $\gamma$-ketobutanes-(2) of the trimethyl-(1,1,3)-tetrahydrobenzenes-(2) and -(3).

In all the above ionone-reductions the keto-group remained intact.

_Pseudo_ionone yielded a tetrahydro- _pseudo_ionone (b. p. 126 to 127° at 14 mm.), of the following constitution:

$$(\text{CH}_3)_2\cdot \text{C} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$$

**Phenols and Phenol-ethers.**

In a paper dealing with the conversion of phenol allylethers into C-allylphenols, L. Claissen\(^1\) describes a phenol which is probably an isomer of eugenol. This is C-allylguaajacol, which Claissen has prepared from guajacol allylether, C$_6$H$_4$(OCH$_3$)(OC$_6$H$_5$) (b. p. 116° at 14 mm.; $d_{150}$ 1,058) by heating it to about 230°. It constitutes a phenol with a pronounced odour of cloves, b. p. 122° at 12 mm., $d_{150}$ 1,071. It differs from eugenol in the m. p. of its phenylurethane (101°, eugenolphenylurethane 95,5°) and of its $\mu$-nitrobenzoate (97°, eugenol-$\mu$-nitrobenzoate 81°). With regard to the constitution of C-allyl guajacol it is thought that the position to which the allyl has migrated must be either the _para_- or the _ortho_-position. If the former, eugenol would be present.

Another instance of the conversion of a phenol-O-allylether into C-allylether is afforded in the case of O-allyl salicylate. Many years ago Scichilone described an acid which he thought to be allylsalicylic acid, C$_6$H$_4$(OCH$_3$)COOH. Singularly enough, this acid took a pronounced violet colour with ferric chloride. In reality, as Claissen has shown, Scichilone was not dealing with allylsalicylic acid but with a mixture of C-allyl and C-propenyl salicylic acids. Scichilone started from methyl salicylate, which he allylated in methylalcohol with potash and allyl iodide. He thus obtained an ester which, before distillation, was no doubt the true O-derivative. But under repeated distillation at ordinary pressure this body became converted into the C-allylated ester, which in addition, when saponified with aqueous potash, became partly transformed into the propenyl derivative. From the potassium-compound of ethyl salicylate with allyl bromide Claissen has obtained pure O-allylethyl salicylate (I) in the form of a colourless oil, b. p. 153° (13 mm.) which did not acquire colour when treated with ferric chloride. Boiling for a brief period with methyl alcoholic potash gave rise to O-allyl salicylate (m. p. 65°). When the O-allylester is subjected to prolonged heating at 230° it gives rise to C-allyl ethylsalicylate (II) (b. p. 142° at 12 mm.) which affords a violet-blue colour with ferric chloride. Free C-allyl salicylic acid melts at 96° and when heated with aqueous caustic potash to 170° is converted into propenyl salicylic acid (III), m. p. 158°. Both acids give pronounced colour reactions with ferric chloride.

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1) *Berl. Berichte* 45 (1912), 3157.
Acids and lactones.

Dehydrocamphoric acid. In a voluminous paper, J. Bredt\(^1\) communicates the result of his research into dehydrocamphoric acid and its derivatives. He has discovered interesting manifestations of isomerism in this acid and its derivatives, and these he explains with the aid of perspective illustrations. Bredt gives detailed directions for the preparation of dehydrocamphoric acid and its derivatives, for the particulars of which we must refer to the original paper. We can only mention here that from the phenylester of chlorocamphoric acid with quinoline a satisfactory yield of phenyl dehydrocamphorate is obtained as a result of the elimination of hydrochloric acid. Free \(d\)-dehydrocamphoric acid has m. p. 202 to 203°; \([\alpha]_D + 118,6^\circ\) (12,98 p. c. solution in chloroform) and \(+113,8^\circ\) (7,83 p. c. solution in absolute alcohol). \((d + l)\)-Dehydrocamphoric acid melts at 228° (from acetic ether).

\[
\begin{align*}
&\text{CH : C \cdot CO}_2\text{H} \\
&\text{C\{(CH}_3\}_2 \\
&\text{CH}_2 \cdot \text{C\{(CH}_3\}\cdot CO}_2\text{H}
\end{align*}
\]

Dehydrocamphoric acid.

When dehydrocamphoric acid is oxidised with nitric acid or potassium permanganate it gives rise to camphoronic acid, and with potassium permanganate it is probable that a keto-acid is formed as an intermediary product. A dibasic acid, probably a dihydroxycamphoric acid, also results from the permanganate-oxidation. When dehydrocamphoric acid is distilled under ordinary pressure it is in part converted into the anhydride of isodehydrocamphoric acid and in part decomposed into camphonenic acid\(^2\) and into a liquid acid of the same constitution, which latter, however, has not yet been obtained in the absolutely pure state. Isodehydrocamphoricanhydride (m. p. 185,5°), when boiled with water, is converted into isodehydrocamphoric acid (m. p. 181 to 182°). The reaction of hydrobromic acid with \(d\)-dehydrocamphoric acid gives rise to two stereo-isomeric hydrobromides of dehydrocamphoric acid, namely, \(d\)-bromo-3-isocamphoric acid (m. p. 232°) and \(d\)-bromo-3-cis-camphoric acid (m. p. 158 to 160°). When reduced with zinc-dust in acid solution, the bomocamphoric acid with m. p. 232° afforded \(iso\)-camphoric acid (\(cis\)-trans-camphoric acid, m. p. 173°) and the bomocamphoric acid with m. p. 158 to 160°, gave \(cis\)-camphoric acid admixed with a little \(cis\)-\(trans\)-acid. The action of hydrobromic acid upon \((d + l)\)-dehydrocamphoric acid led to \((d + l)\)-bromo-3-\(iso\)-camphoric acid (m. p. 239 to 240°), which, when reduced with zinc dust, was converted into \((d + l)\)-\(cis\)-\(trans\)-camphoric acid. Komppa’s designation "\(\beta\)-bromocamphoric acid" is not singular in its meaning, because there must be two \(\beta\)-bromocamphoric acids in isomeric position. The compound might with equal appropriateness be called \(\gamma\)-bromocamphoric acid, and for this reason Bredt proposes the designation bromo-3-camphoric acid. Bromo-3-\(cis\)-

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\(^1\) Liebig’s Annalen 396 (1913), 26.  
\(^2\) For the nomenclature see below.
camphoric acid, when boiled with soda-liquor, gives rise to hydroxy-3-camphoric acid lactone. The bromo-3-camphoric acid with high m. p. was decomposed by prolonged heating of its neutral soda-salt in aqueous solution, giving rise to hydroxy-3-iso-camphoric acid and camphonic acid. When dehydrocamphoric acid chloride is heated with bromine in a sealed tube there ensued a reddish-coloured syrupy mass, which was converted by decomposition with sodium carbonate into an acid containing two hydrogen atoms fewer than laurolenic acid\(^1\) and which for this reason was called dehydrolaurolenic acid.

For the nomenclature of substituted camphoric acids, Bredt has adopted the notation of the cyclic carbon atoms, as previously drawn up by von Bayer and more recently by Grignard\(^2\). In common with camphor, camphoric acid contains the camphocean-(trimethyl pentamethylene-)ring (I)\(^3\). The camphoric acid derivatives substituted for the two gem. methylenes Kipping denotes with the letter \(\pi\). For the designation of those derivatives of camphoric acid in which the substitution occurs in the third methyl in end-position, Bredt proposes the letter \(\Omega\). As an example of this notation he cites the four monobromocamphoric acids which are known up to the present. These are bromo-3-camphoric acid (II) to which reference has been made above, bromo-4-camphoric anhydride (III), \(\pi\)-bromocamphoric acid (IV)\(^4\) and the acid which has been obtained by Armstrong and Lowry\(^5\) from the oxidation of \(\beta\)-bromocamphor, which possibly may represent the \(\Omega\)-bromocamphoric acid (V).

\[
\begin{align*}
(\text{I}) \text{ Camphocean ring.} & \quad (\text{II}) \text{ Bromo-3-camphoric acid.} & \quad (\text{III}) \text{ Bromo-4-camphoric anhydride.} \\
\text{CH}_2 \cdot \text{CH}_3 \\
\text{C(CH}_3)_2 \\
\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_3 & \quad \text{CH}_2 \cdot \text{CBr} \cdot \text{CO} & \quad \text{CH}_2 \cdot \text{CBr} \cdot \text{CO} \\
\text{C(CH}_3) & \quad \text{CH}_2 \cdot \text{CO}_2 \text{H} & \quad \text{C(CH}_3)_2 \text{(}\pi\text{)} & \quad \text{C(CH}_3)_2 \text{O} \\
\text{CH}_2 \cdot \text{C} \cdot \text{CO}_2 \text{H} & \quad \text{CH}_3(\Omega) & \quad \text{CH}_2 \cdot \text{C} \cdot \text{CO}_2 \text{H} & \quad \text{CH}_3(\Omega) \\
\text{H}_3 \text{C} & \quad \text{CH}_2 \text{Br} & \quad \text{CH}_2 \text{Br} & \quad \text{CH}_2 \text{Br} \\
\text{CH}_2 \cdot \text{C} \cdot \text{CO}_2 \text{H} & \quad \text{CH}_3 & \quad \text{CH}_2 \cdot \text{C} \cdot \text{CO}_2 \text{H} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
(\text{IV}) \pi\text{-Bromocamphoric acid.} & \quad (\text{V}) \Omega\text{-Bromocamphoric acid.} 
\end{align*}
\]

In an article on new methods of preparing camphonenic acid (\(\gamma\)-lauronolic acid) and its relations to laurolenic acid (lauronolic acid), which has been published almost simultaneously with the above, Bredt\(^6\), while as far as possible adhering to existing conditions, has removed a maze of designations which has already given rise to continual confusions and errors, and would have continued to do so. This applies principally to the designations laurolenic acid and campholactone, which are henceforth abolished. Bredt starts from the following points of view: — At the present time we have knowledge of two series of unibasic unsaturated acids derived from camphoric acid. To the one series belong camphonenic acid and laurolenic acid. (The latter,

\(^{1}\) For the nomenclature see below. — \(^{2}\) Comp. Report October 1912, 143. — \(^{3}\) Liebigs Annalen 299 (1897), 162. — \(^{4}\) Kipping, Journ. chem. Soc. 69 (1896), 918. — \(^{5}\) Ibidem 81 (1902), 1467. — \(^{6}\) Journ. f. prakt. Chem. II. 87 (1913), 1.
being an unsaturated compound, would be more appropriately called laurolenic acid.) Both of these still contain, linked to the tertiary carbon atom, the carbonyl of camphoric acid. The other series, with a carbonyl in secondary position, includes campholytic acid and isocampholytic acid (β-campholytic acid). We now know positively that the bodies formerly known as lauronolic acid, isolauronolic acid, bihydrolaurolactone, and isobihydrolaurolactone do not stand in a uniform relationship towards each other, that is to say they are not merely differentiated by the different positions of the double-bond, as was formerly assumed. They exhibit different carbon-skeletons, inasmuch as camphonenic acid (VII) (iso- or γ-lauronolic acid) still contains the gem. dimethyl-radical of camphoric acid, whereas laurolenic acid (lauronolic acid) (XV) does not. Hence, camphonenic acid is closely related to dehydrocamphoric acid (VI) on the one hand and to camphonic or camphonolic acid (XIII and XI) on the other. We reproduce below the atomic formulæ of the principal representatives of these two series of compounds, so far as they are at present known.


- Dehydrocamphoric acid. (VI)
- Camphonenic acid. (VII)
- Camphonanic acid. (VIII)
- Bromocamphonanic acid. (IX)
- Aminocamphonanic acid. (X)
- Camphonolic acid. (XI)
- Camphonololactone. (XII)

2. Laurolene and Laurolane series.

- Laurolene. (XIV)
- Laurolic acid. (XV)
- Laurolanic acid. (XVI)
- Laurolactic acid. (XVII)
- Laurolactone. (XVIII)

1) Comp. Journ. f. prakt. Chem. II. 88 (1911), 400.
Subjoined are a few of Bredt's designations, together with their synonyms:

<table>
<thead>
<tr>
<th>Bredt's nomenclature</th>
<th>Synonym</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camphonolic acid</td>
<td>Hydroxyauronic acid ¹)</td>
</tr>
<tr>
<td>Laurolonic acid</td>
<td>Hydroxy acid of campholactone ²)</td>
</tr>
<tr>
<td>Camphonololactone</td>
<td>Iso-campholactone ³)</td>
</tr>
<tr>
<td>Laurolanic acid</td>
<td>Dihydrolauronic acid</td>
</tr>
<tr>
<td>Laurolactone</td>
<td>Campholactone (Bihydrolaurolactone)</td>
</tr>
<tr>
<td>Laurolenic acid</td>
<td>Lauronic acid</td>
</tr>
<tr>
<td>Camphonenic acid</td>
<td>γ-Lauronic acid</td>
</tr>
</tbody>
</table>

Bredt's nomenclature has this advantage, that it shows at a glance to what common class the compounds belong, further, that it gives due weight to the characteristic ultimate syllables of the Geneva nomenclature and that in registration the compounds which belong together can be placed one below the other.

In the experimental part of his paper Bredt reports on the preparation of camphoric acid from dehydrocamphoric acid by readily-proceeding reactions, which, at the same time, left no doubt as to their constitution. From dehydrocamphoric acid he obtained by dry distillation, in addition to isodehydrocamphoric anhydride, camphoric acid m.p. 155 to 156° (from acetic acid). He also obtained camphoric acid from dehydrocamphoric acid hydrobromide by boiling the neutral sodium salt of the cis-trans-acid with m.p. 232° (see above) in aqueous solution in a reflux condenser, thereby obtaining in the principal place a hydroxy acid and up to 10 p.c. camphoric acid, the latter being separated from the former by steam-distillation. When camphoric acid is oxidised with nitric acid or with potassium permanganate it gives rise to camphoronic acid.

Finally, Bredt, in collaboration with A. Amann ⁴), reports on a new method of preparing laurolenic acid (lauronic acid) from bromocamphonic acid, and on the resolution of camphanic acid in an electrical reflux-heater under diminished pressure. When bromo-4-camphonic acid is boiled with alkali it is partly transposed into laurolenic acid (Woringer's lauronic acid). Laurolenic acid may also be obtained by heating chlorocamphoric anhydride with soda solution, in which case a mixture of laurolenic acid and camphanate of sodium is formed. In conclusion the authors describe the preparation of laurolenic acid by distilling camphamic acid in a reflux condenser under diminished pressure in an apparatus which has been constructed on the model of the vacuum-distilling apparatus with electrically-heated delivery arrangement previously described by Bredt and van der Maaren ⁵). The calcium salt of laurolenic acid which had been prepared by different methods was analysed, and its optical rotation determined. The latter varied in the different preparations from $[\alpha]_{D20} + 181.3^\circ$ to $[\alpha]_{D20} + 195.2^\circ$.

Dihydrocamphoceiveinic acid. It would be expected that when dihydrocamphoceiveinic acid (camphenilollic acid) is oxidised with permanganate, a hydroxy acid, and from the latter the corresponding lactone (dimethyl norcampholide), would be formed. But from a paper by S. V. Hintikka ⁶) we gather that such is not the case, but that on the contrary the camphenilollic acid is split up in a far-reaching manner,

the reaction giving rise to acetic acid and to several other acids, among which in all probability, is butyric acid.

On the reduction of cinnamic acid see p. 134.

Dihydrocarvenolide. Some time ago we recorded the reduction, by Wallach, of the lactone \( i \)-carvenolide \( C_{10}H_{14}O_2 \) to dihydrocarvenolide by Paal’s method\(^1\). Since that time Wallach has continued his investigations\(^2\) and has discovered that it is possible to reduce the \( D-l \)-carvenolide obtained from \( d \)-carvone to \( D-l \)-dihydrocarvenolide (m. p. 50 to 51\(^{\circ} \)), a body which is identical with dihydropulegenolide of the same m. p.\(^1\). Seeing that the presence of a pentacyclic ring in pulegenolide, or rather in its parent-substance, pulegenic acid, is a proved fact, it follows that carvenolide must likewise contain a pentacyclic modification, that is to say, that when carvone tribromide is converted into carvenolide, a ring-displacement occurs. Wallach has furthermore observed that pulegenolide is not inactive, as was formerly believed to be the case, but faintly active. It is remarkable that the activity becomes more pronounced after the reduction of the body.

In the course of the preparation of \( i \)-carvenolic acid (m. p. 135 to 136\(^{\circ} \)) from \( i \)-carvenolide by boiling with alkali, an isomeric acid, m. p. 104 to 105\(^{\circ} \), was detected as a by-product. Wallach differentiates between this compound \( \beta-i \)-carvenolic acid, and that with a higher b. p. (\( \alpha-i \)-carvenolic acid.) When melted with potash, carvenolic acid yields an acid with 7 carbon-atoms, probably a \( \Delta^1 \)-methylpentene carboxylic acid. There is an easier way of preparing pulegenolic acid than from pulegenolide, namely from the brominated lactone of pulegenic acid by boiling with sodium methylate. Dihydrocarvenolic acid was prepared from \( i \)-, \( d \)- and \( l \)-dihydrocarvenolide by saponification with potash-liquor. It is identical with the acid obtained from dihydropulegenolide. When subjected to slow dry distillation it yields a hydrocarbon and an acid, which may perhaps be identical with pulegene and pulegenic acid. An acid of the same constitution as pulegenic acid is also formed when \( d \)-dihydrocarvenolic acid is melted with caustic potash at about 130\(^{\circ} \), but this acid does not appear to be identical with pulegenic acid. Its amide has m. p. 115\(^{\circ} \) and is laevorotatory, whereas the amide of pulegenic acid (m. p. 121\(^{\circ} \)) is dextrorotatory. The amide of pulegenic acid (\([\alpha]_D +29,05^{\circ} \)) is very difficult to reduce, which may be explained on the assumption that it contains a semicyclic double-bond. This bond appears to unite with hydrogen with difficulty, as has, for instance, been demonstrated already in the case of \( \beta \)-fencholenic acid\(^3\), and as applies also to \( \beta \)-campholenic acid. The saturated amide \( C_9H_{12}CONH_2 \) which is obtained from pulegenic acid amide is only very faintly dextrorotatory (\([\alpha]_D +4,847^{\circ} \)).

Bergaptene and xanthotoxin. It will be remembered that H. Thoms\(^4\) has ascertained the presence, in the peel of \( Fagara xanthoxyloides \), of bergaptene and xanthotoxin. Recently, in collaboration with E. Bætcke\(^5\), Thoms has elucidated the constitution of bergaptene. At an earlier date Pomeranz had been led to the belief,

\(^{1}\) Comp. Report October 1911, 126. \(^{2}\) Liebigs Annalen 392 (1912), 49. \(^{3}\) Comp. Report April 1911, 165. \(^{4}\) Berl. Berichte 44 (1911), 3325; Report April 1912, 80. \(^{5}\) Berl. Berichte 45 (1912), 3705.
as a result of his own researches, that bergaptene is a coumarin-coumarone derivative, and had suggested that one of the formulae I, II and III, set forth below might apply to it. A. Tschirch\(^1\) assigns to bergaptene formula II, but without adducing evidence for his belief. Thoms has now acquired the conviction that the structure shown in formula I is the correct one for bergaptene. In collaboration with Bætcke he has reduced nitrobergaptene to amino-bergaptene (m. p. 198\(^\circ\)) by warming it with tin and hydrochloric acid, and from the reduced substance, by oxidation with sodium bichromate and sulphuric acid in the cold, he obtained a body C\(_{11}\)H\(_{16}\)O\(_5\), crystallising in gold-coloured crystals, m. p. 248 to 250\(^\circ\). It contained neither methoxyl nor nitrogen, hence it is clear that in the process of oxidation the amino- and the methoxyl-groups were split off from the amino-bergaptene, and were each replaced by one oxygen atom. Seeing that as a rule the elimination of such groups and their replacement by oxygen takes place in the para-position, it may be concluded that, since bergaptene is a phloroglucin-derivative, its substitution-products are arranged as shown in formula I.

By a similar method the nitrooxanthotoxin was converted from primarily-produced aminoxanthotoxin (m. p. 236\(^\circ\)) into the same quinone, m. p. 248 to 250\(^\circ\); hence xanthotoxin possesses the constitution expressed in formula V. When quinone is boiled with sulphurous acid it yields the corresponding hydroquinone, of which the diphenylurethane melts between 229 and 230\(^\circ\) and the diacetyl derivative between 208 and 209\(^\circ\).

![Formulae](attachment:formulae.png)

**IV. Quinone from bergaptene and xanthotoxin.**  
**V. Xanthotoxin.**

**Oxides.**

A few years ago we referred to a paper by N. Prilechajeff\(^2\) on the preparation of the oxides and peroxides of various terpene bodies. Afterwards we were able to establish the presence of one of these oxides, viz., linalool oxide\(^3\), in linaloe oil. Prilechajeff\(^4\) has now published full particulars of the properties of these interesting bodies, and the following particulars are taken from his paper:

Geraniol monoxide absorbs water in the presence of traces of an acid, giving rise to a glycerol C\(_{10}\)H\(_{17}\)(OH)\(_3\): b. p. 204 to 206\(^\circ\) (19 mm.), d\(^\text{19}^\text{6}\)\(_{15}\) 1,0486, n\(_D\)\(_{19}^\text{8}\) 1,4935; triacetate,

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\(^1\) Handbuch der Pharmacognosie, Leipzig 1912, Vol. II, p. 872. — \(^2\) Berl. Berichte 42 (1909), 4811; Report April 1910, 153. — \(^3\) Report October 1912, 78. Our statement that we had isolated linalool oxide both from Mexican and from Cayenne linaloe oil is founded upon an error. As a matter of fact we have detected it in Mexican linaloe oil only. — \(^4\) Journ. russ. phys. chem. Ges. 44 (1912), 613; Chem. Zentralbl. 1912, II. 2090.
b. p. 208° (25 mm.), \(d^{16}_\text{deg} = 1,0619\). Geraniol dioxide, in the presence of traces of an acid, yields a mixture of two compounds, one a crystalline product, \(C_{10}H_{17}O(OH)\_2\_2H_2O\), m. p. 94,5 to 95,5°, and the other a liquid portion. The crystalline product, after being dried, was split up into two compounds by recrystallisation from glacial acetic ester under exclusion of moisture, \textit{viz.} 1. A compound \(C_{10}H_{17}O(OH)\_3\), m. p. 145 to 146° and 2. a compound of the same constitution but with m. p. 163 to 164°. The first-named compound is a monohydrate of geraniol dioxide and with acetic anhydride forms an ester \(C_{10}H_{17}(OCOCH)\_3\): b. p. 189,5 to 190° (14 mm.), \(d^{16}_\text{deg} = 1,1253\). The liquid portion which is formed in the hydration of geraniol dioxide boils between 197 and 201° (14 mm.), but it does not appear to be a uniform body. Prilechajeff now ascribes to linalool monoxide somewhat different properties than those which he had enumerated for it on a previous occasion. He gives b. p. 197 to 198° (758 mm.), \(d^{16}_\text{deg} = 0,9520\), \(n_{D16} = 1,45567\). The constants\(^1\) determined by us at the time for preparations derived from Mexican linaloe oil were as follow: b. p. 193 to 194°, 63 to 65° (4 mm), \(d^{16}_\text{deg} = 0,9431\) to 0,9442, \(\alpha_p = -5°25'\) to \(-5°46'\), \(n_{D16} = 1,45191\) to 1,45221. Prilechajeff attempted to hydrate the linalool monoxide, but without success. When heating it with highly dilute hydrochloric acid to 150° he obtained a product with an odour of camphor, b. p. 120 to 122° (25 mm.), \(d^{16}_\text{deg} = 0,8576\); \(n_{D16} = 1,5038\); semicarbazone, m. p. 138,5° which rapidly becomes oxidised into a gum-like mass when exposed to air. Linalool monoxide when treated with acetic anhydride yields a liquid with an odour of bergamot oil, b. p. 118 to 119° (25 mm.): \(d^{16}_\text{deg} = 0,9770\), \(n_{D16} = 1,44972\). Prilechajeff gives the sp. rotation of linalool dioxide as \([\alpha]_D + 5,3°\); \(n_{D16} = 1,46170\). When hydrated it forms a glycerol oxide which with acetic anhydride yields a compound \(C_{10}H_{17}(OH)(OCOCH)\_3\): b. p. 207 to 209° (20 mm.) \(d^{16}_\text{deg} = 1,114\), \(n_{D16} = 1,4531\). The oxide of linalyl acetate, \(C_{10}H_{17}O\_2\_COCH\_3\), boils between 138 and 139° (25 mm.): \(d^{16}_\text{deg} = 0,9742\), \([\alpha]_D = -2,58°\), \(n_{D16} = 1,44847\). It absorbs water energetically, giving rise to a compound \(C_{10}H_{17}(OH)(OCOCH)\_3\), b. p. 171 to 175° (20 mm.). After saponification of this ester there is formed a body \(C_{10}H_{17}(OH)\_3\): m. p. 54 to 55°, b. p. 177 to 180° (15 mm.). On the present occasion Prilechajeff gives the following data for citral monoxide: b. p. 144,5 to 145,5° (20 mm.), \(d^{16}_\text{deg} = 0,9679\), \(n_{D16} = 1,47848\). The glycol which is formed when citral oxide is hydrated has \(d^{16}_\text{deg} = 1,0335\). Treatment with moist silver oxide gives rise to an acid \(C_9H_{14}(OH)COOH\), b. p. 176 to 180° (19 mm.) with acetic anhydride the glycol forms a compound \(C_{10}H_{16}O_3(COCH)\_3\), b. p. 205 to 207° (15 mm.). When it was attempted to prepare citral dioxide, a decomposing oxidation ensued and a carbon-atom was split off, giving rise to a body \(C_9H_{14}O_2\), b. p. 114 to 115° (25 mm.), \(d^{16}_\text{deg} = 0,9419\), \(n_{D16} = 1,43728\). The hydrate of this body boils between 161 and 162° (25 mm.), \(d^{16}_\text{deg} = 1,0573\), \(n_{D16} = 1,4710\).

**Nitrogenous bodies.**

Sinigrine. According to Gadamer's investigations\(^2\) the glucosides of mustard oil are in all probability derived from a hypothetic alkyliminothiol carbonic acid, possessing the general formula \(R\_N: C(SH)(OH)\). Thus, in his opinion, sinigrine possesses the structure (shown in formula I), of an allylimino thiol carbonic acid, of which the hydroxyl is esterified with the residual acid (potassium bisulphate), while the sulphohydryl occurs in an ether-like combination with glucose.

As the formula of sinigrine is at present only of a hypothetical character, W. Schneider\(^3\) has undertaken to synthetise compounds of type I and to compare the chemical behaviour

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1) \textit{Report October 1912}, 78. — 2) \textit{Arch. der Pharm.} 235 (1897), 47; \textit{Berl. Berichte} 80 (1897), 2322, 2328. — 3) \textit{Berl. Berichte} 48 (1912), 2961.
of the bodies thus obtained, in particular towards enzymes, with the natural glucosides of mustard oil. It has long been known that aromatic sulpho-urethanes, as for instance phenyl sulpho-urethane, (II) are pronounced acids, inasmuch as they react in the sense of their tautomeric, acid, form (III). Accordingly, with heavy metals, they yield stable salts from which ethers alkylised with sulphur are obtained (IV).

In view of the fact that, so far, purely aromatic isosulphocyanates have not been observed in nature it was interesting to determine whether sulpho-urethanes aliphatically substituted in nitrogen could be converted by an analogous method into esters of iminothiol carboxinic acid. With this object in view Schneider took as his starting point allyl sulpho-urethane, which is generated from allyl isosulphocyanate and an excess of alcohol, b.p. 115 to 118° at 14 mm. In contradistinction to its aromatic analogues, this body does not perceptibly dissolve in aqueous alkalies, but with ammoniacal silver solution it yields a fairly stable silver salt (V) in which according to all appearance the silver is in combination with sulphur. This salt, when heated with ethyl iodide in a sealed tube, is converted into the allyl sulpho-urethane ethylether, allylimino thiol diethyl carbonate (VI). When boiled with an alkaline solution of lead oxide this body remains stable, in contradistinction to sulpho-urethane, which immediately forms sulhide of lead. Furthermore, when heated with sulphuric acid, it splits off mercaptane, hence the newly-introduced ethyl is certainly combined with the sulphur and not with the nitrogen. Schneider hopes, later on, to be able to report on the behaviour of the synthetic ester towards silver nitrate and enzymes.

\[
C_6H_5N : C\cdot\underline{\text{S}} \cdot C_6H_{11}O_3 \\
\text{(I) Sinigrine.}
\]

\[
C_6H_5 \cdot \text{NH} \cdot \text{CS}(\text{OC}_2\text{H}_5) \quad \text{↔} \quad C_6H_5 \cdot \text{N} : \text{C(SH)}(\text{OC}_2\text{H}_5)
\]

\text{(II) Phenylsulpho-urethane.} \quad \text{(III) Tautomeride.}

\[
\text{(IV)} \quad C_6H_5N : \text{C(SAg)}(\text{OC}_2\text{H}_5) + \text{CH}_3] = C_6H_5 \cdot \text{N} : \text{C(SCH}_3)(\text{OC}_2\text{H}_5) + \text{AgJ}
\]

\text{Silver salt of phenylsulpho-urethane.} \quad \text{Ether alkylised with sulphur.}

\[
\text{(V)} \quad C_6H_5 \cdot \text{N} : \text{(CSAg)}(\text{OC}_2\text{H}_5)
\]

\text{Silver salt of allylsulpho-urethane.} \quad \text{(VI) C}_6\text{H}_5 \cdot \text{N} : \text{C(SC}_2\text{H}_5)(\text{OC}_2\text{H}_5)

\text{Allyl iminothiol diethyl carbonate.}

A sulphone-mustard oil from the seed of Erysimum Perofskianum is described on p. 52 of the present Report.

Alkylidene hydrazines. On the present occasion we are again able to report on the resolution of alkylidene hydrazines\(^1\). Kishner\(^2\), in continuing his previous investigations, has found that when menthyldiene hydrazine is heated in the presence of pieces of platinized porous tile, menthane is formed: b.p. 171°, d\(^\circ\) \text{p} 0,7963. Menthylidene hydrazine is obtained by heating menthone and hydrazine hydrate: b.p. 248 to 249°. By analogous method isothujidene hydrazine is formed from thujone and hydrazine hydrate. When isothujidene-hydrazine is heated with potassium hydroxide, the azine of isothujane results; when boiled with 20 p.c. sulphuric acid isothujane is

regenerated. Carvylidene hydrazine was not obtained in the pure state, as decomposition set in during the distilling-process.

Phenol bases. In continuing his syntheses in the fatty-aromatic series\(^1\)\) \(^2\) J. von Braun, in collaboration with H. Deutsch\(^3\)\), has prepared a few phenol bases, namely \(o\)- and \(p\)-hydroxyphenylpropyl dimethylamine, \(p\)-hydroxyphenylbutyl methylamine, and \(p\)-hydroxyphenylamyl dimethylamine, with many derivatives, among which we may briefly refer to homotyrosol (\(p\)-hydroxyphenylpropylalcohol). This body, which melts at 55°, is physiologically neutral, in contradistinction to tyrosol. Its dibenzoyl derivative has m. p. 72°.

\(^1\) Comp. Report October 1912, 164.  \(^2\) Berl. Berichte 45 (1912), 2504.