INDUSTRY OF ARTIFICIAL PERFUMES.*

By Justin Dupont.

Among the discoveries which have passed from the chemical laboratory into the domain of industry, some of the most fruitful have been those connected with the production of artificial perfumes. Of course, this industry, whose markets are naturally restricted, cannot be compared with that of artificial coloring matters, whose annual production is estimated as amounting to hundreds of millions of francs. Yet, as much from its successful practical results as from the ingenuity of its researches, this industry deserves attention.

M. Jungfleisch, the distinguished professor of the school of pharmacy (Paris), thus characterizes it: "Among the industries created in France within the last twelve years, not the least original is that of which M. de Laire has been the initiator, even if it does not involve the most extended theoretical investigations; these frequently impose, under the most varied forms, the task always delicate, of transforming a laboratory experiment, always delicate, into a manufacture suitably regulated."

Up to 1876, the time when Mons. G. de Laire, already well known from his interesting work on coaltar coloring matters, established at Grenelle the first factory for the manufacture of vanillin, the chemical products employed in perfumery and confectionery were limited to nitrobenzol (oil of mirbane), benzoic aldehyd (oil of bitter almonds) and certain ethers having fruit odors. That date is the commencement of the history of this interesting industry.

The artificial production of a perfume can be obtained in two very different ways. In certain cases, where the odorous properties have been separated in a state of purity from the natural material, identically the same compound with all its physical, chemical and organoleptic properties can be prepared. This has been accomplished in obtaining "vanillin," the principal odor of the vanilla pod; "cumarin," the principle of the tonka bean; cinnamic aldehyd, the principle of the oil of cinnamon, etc. At other times compounds possessing intense and characteristic odors, strikingly resembling those of the natural products, have been produced, although no chemical analogy has been established between them. This is the case with the artificial musk, ionone, isoeugenol (odor of carnations), phenyl acetic aldehyd (odor of hyacinth), terpineol (lily of the valley), piperonylic aldehyd (heliotrope), and other perfumes.

Contrary to experience in several branches of chemical industry, that of artificial perfumes created in France by M. de Laire at the same time as in Germany by Tieman and Haarman, has never been in danger of failure, and the recent exhibit of De Laire & Co. made a good showing beside the German exhibit. We shall briefly describe some of these products:

Vanillin.—The synthetic reproduction of vanillin was really the beginning of the industry of artificial perfumes. Tieman & Haarman first effected this result. They resorted for this purpose to coniferin, the glucosid found in the sap of the pine.

Coniferin divides, under the dehydrating reagents, into glucose and coniferylic alcohol, alcohol of which vanillin is the aldehyd. By oxydizing at once the coniferylic alcohol, vanillin is obtained.

The first vanillin offered to commerce was prepared in small quantities by that process. From the scarcity of the coniferin and the limited yield, the price was very high, about 8,000 to 9,000 francs per kilogram. Such a method could not provide a popular product. Thus it was rapidly abandoned.

In the course of their researches Tieman and Haarman, later M. de Laire, established the close relationship of chemical constitution existing between vanillin and the phenol of oil of cloves, eugenol.

This really started the industrial manufacture of vanillin. A preparation is made, suitably oxidized, either of eugenol or its isomerid, isoeugenol, or some special derivatives of these, selected as indicated by the best results. All these substances have been covered by numerous patents of Haarman and Tieman in Germany, and of De Laire in France.

The artificial vanillin came rapidly into favor. The perfumer and the confectioner found speedily the advantage in using a definite compound, easily measured, always possessing the same odorous powder, and with equal intensity, costing much less than the natural product. The gradual reduction in price made the vanilla product popular. It could be employed in such articles as chocolates, confectionery, biscuits, whereas formerly it had been reserved for articles of luxury.

This reduction of the price of vanillins is a characteristic proof of the industrial activity of our time. Before the assured success of the product numerous processes were attempted which might be substituted for the patented methods. Then patents were taken out by Boehringer, by Meister, Lucius and Bruning, Heinhorn, Majest, Schering, the Rhone Company, and others. In the face of this boundless competition the price of a kilogram of vanillin, which was in 1880 about 2,000 francs, in 1890, 850 francs, fell that year to 100 francs. The successive improvements had thus brought down the price.

Heliotropin.—Another important product is piperonylic aldehyd, or heliotropin. It is obtained by oxidizing safrol, or better, its isomerid, isosafrol. Safrol is a special product, which forms the greater part of the oil of sassafras. Heliotropin has a considerable use in perfumery. Combined with vanillin it forms the base of the extracts of heliotrope. Its preparation, at least from safrol, has never been protected by patent, so that its price has fallen more rapidly than that of vanillin. Offered to commerce in 1879 at the price of about 3,800 francs, in 1890 it brought only 375 francs, and to-day it sells for about 35 francs.

Cumarin does not, perhaps, appropriately have a place here, because it is not artificially manufac-

*Oil, Paint and Drug Reporter. From La Nature.

tured, but is the extract of natural products. Since 1825 it has been known as the odorous constituent of the tonka bean. It exists, besides, in a great number of vegetables—in the flower of the honey-lotus, the fragrant "woodruff," in a plant very abundant in Florida, the liatrix odoratissima, called in that section "deer-tongue."

The chemical study of cumarin has been exhaustive. Its conclusion is the synthetic production of the substance by means of salicylic aldehyd. It was thus prepared up to the time of the discovery of liatrix odoratissima. Possibly, if the original material is insufficient, or it can be prepared from salicylic acid at a price sufficiently low, chemistry eventually may have an advantage over nature.

Cumarin is an excellent product, of great stability in presence of the alkalies, which renders it valuable for the soap industry. The perfumers use it principally for compounding the extract "new-mown hay."

Terpineol.—This can be taken as the type of artificial perfumes. It is made by dehydrating terpin hydrate, derived immediately from turpentine. Studied at first by List, Tanret, Bouchardat, it was industrially prepared and introduced into perfumery in 1889 by De Laire & Co.

In solutions suitably diluted, terpineol has the fresh odor of lilac or lily of the valley. It has also been found in the natural state in several oils of flowers. Its price is low, which allows its use in preparations of moderate price. It is unaffected by the action of alkalies, and the soap-makers have utilized it extensively.

Artificial Musk.—The odorous substances of animal origin, musk, ambergris, civet, etc., have specific qualities which are of the greatest assistance to the perfumer. These qualities have been long known and employed. If musk or ambergris is added to a bouquet of oils of flowers, not only is a special increase of strength given to it, but it acquires such a tenacity that a handkerchief thus perfumed preserves the fragrance for a long time, while that of the vegetable oils evaporates rapidly. Unfortunately, the use of these substances has been restricted by their high price. Analytical researches on such substances as musk or ambergris requires a great outlay without certainty of success. The problem does not appear so far to have been seriously entertained; the odoriferous principle of musk or of ambergris has never been extracted in the form of a definite compound. It is not even known whether the odor is due to definite compounds; synthetic reproduction appears therefore to be quite distant.

Happily, chemistry has again come to the aid of the perfumer. For a long time the fact has been casually remarked that the action of nitric acid upon oils resulting from certain dry distillations gives rise to products of a musky odor. Nevertheless, no industrial application was incited until 1889, when M. A. Baur took out a patent for the manufacture of a new compound designed to replace the musk of animal origin in perfumes. This substance was trinitrobutyl-toluene, a definite compound, endowed with an intense, musky odor, having a similar and even superior tenacity to that of natural musk. This worked a complete revolution in the technics of perfumery. At the same time the reproduction of vanillin was popularizing that perfume. Baur's discovery allowed the perfumer to employ in his preparations a substance endowed with the specific qualities of musk.

Trinitro-butyl-toluene, manufactured in France by M. De Laire & Co., was exhibited at the exposition of 1889, and at once achieved a great success. Since that time, M. Baur, continuing his researches, has obtained a homolog of his first artificial mark, the trinitro-butyl-xylene. This is the substance most generally used by the perfumers, its odors being less intense and sweeter.

Ionone.—This oil of artificial violet is not less important than that of artificial musk. Its discovery in 1895 was the fruit of long and patient researches, an example of masterly work in the domain of chemistry.

Extraction of the violet aroma, so soft and delicate, has always been an arduous task. Therefore extracts from the violet have been compounded mostly with concrete oil or with the alcoholic tincture of iris root, whose odor approaches that of the violet.

Tieman, prematurely cut off from scientific work, and De Laire undertook experiments on the perfume of the violet, which were continued more than ten years, resulting in 1895 in the discovery of ionone by Tieman and Kruger. These savants having extracted in the pure state "irone," the odoriferous principle of the root, ascertained precisely its composition and its chemical nature. To reproduce it artificially they had recourse to a natural aldehyd, citrol, forming the principle of the oils of lemon and verbena of the Indies (lemon-grass). By condensing citrol with acetone in presence of an alkaline reagent, such as a baryta solution, then submitting the intermediary product obtained to the action of dilute sulfuric acid, which produces a special isomerism, Tieman & Kruger obtained, not the irone itself, but an isomer, the ionone. This substance, in a state of extreme dilution, possesses strikingly the characteristic odor of the violet. The subsequent study of this compound or other related derivatives of citral form an important chapter in this branch of chemistry. From a practical standpoint, ionone has been of considerable utility to the perfuming industry. Its use is now general.

Besides these compounds, the most important of artificial perfumes, are ranked other products which have been advantageously used in artificial perfumery. These are anise aldehyd or aubepin, produced by oxidation of anise oil; pheny-lactic aldehyd, having the odor of hyacinth; acetophenone and benzophenone; the benzoates, cinnamates, salicylates of methyl and ethyl, the methylic and ethylic ethers, betanaphthol, and others.

Such are, in brief, the stages of this industry, in existence scarcely a quarter of a century. Many questions remain to be solved. The number and attainments of the investigators who are making them their sole study, justify us in constantly expecting new revelations.

DUMB CLINICAL THERMOMETER.—A member of the Zurich Medical Society has devised a self-registering clinical thermometer on which there were no degree marks. The instrument could be left with the patient's family to take the temperature in the absence of the physician, and the latter could then read it by means of an attachable scale of glass or metal.