Perfumery materials industry in Poland:
Its organization and recent investigations

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As is well known, great developments in the chemical industry marked the second half of the nineteenth century. A number of Polish scientists, including Jakub Natanson, Marceli Nencki, Stanislaw Kostanecki, Zygmunt Wróblewski, Karol Olszewski, Bronislaw Radziszewski, Maria Sklodowska-Curie, and others took part in this development and helped to build the modern chemical industry.

Because of the unfavorable social and political conditions at that time, however, it was not possible for Poland to profit from the potential of its own scientists in this industrial development. As a result of successive partitions of the country, Polish territories had been annexed by three foreign powers, and these territories were made dependent on the invaders' states. Consequently, establishing any national industry was difficult, if not impossible.

Even with the recovery of national independence in 1918, the situation was no more favorable since the industry remained in the hands of foreign capital. Under these conditions, Poland missed the chance of an early start in the chemical industry, and still lags behind other countries.

Before World War II, the perfumery industry in Poland depended mostly on imported products, such as finished odoriferous compositions, essential oils, synthetic compounds, and odoriferous bases. There was no production of raw perfumery materials in Poland at that time, with the exception of small quantities of essential oils obtained from indigenous plants.

Nationalization of industry in Poland after World War II included the perfumery and cosmetics industry. The first period in the development of this industry was characterized by the import of raw materials, mostly from France, but the increasing demand for perfumery materials provided the impulse to establish a national industry in this area. Toward this purpose, a plant was constructed in Warsaw in 1956. During the period from 1960 to 1964, this plant was enlarged and modernized. Now under the name of Perfumery Synthetic Factory, "Pollena-Aroma," this is one of sixteen plants belonging to the Industrial Association of Detergents and Cosmetics (Zjednoczenie Przemyslu Chemii Gospodarczej), which is organized under the Ministry of the Chemical Industry.

Almost the entire production of cosmetics, perfumery products, washing products, detergents, and household chemicals falls under the control of this association. The Pollena-Aroma plant produces synthetic perfumery materials, resinoids, and perfumery compositions for the association and also for other customers in Poland. These products are all manufactured according to the factory's own formulas. The perfume compositions are furnished to the other factories of the group, which, in addition to their activity in the field of cosmetics, produce perfumes, flower waters, eau de cologne, and other perfumery products. The most important perfumery compositions are described in Table I.

Table I

Pollena-Aroma-produced Compositions

Product	Odor
Prastara	characteristic eau de cologne
Condella	fantasy with a chypre note
Egzotyka	very fresh, sensual, elegant
Lawenda	fresh, pure scent of lavender
Market	floral, dominant note of hyacinth
Sako	herbal with a fruity note
Narcilla	fantasy of flowers, with a light note of narcissus, sweet, powdery, and simultaneously fresh
Premier	fantasy of lemon and orange, fresh, typically male
Sawa	fantasy, woody, powdery with a dominant sweet note of lily of the valley and rose
Wirtu	fresh lemon and orange with a note of jasmin and rose

It should be mentioned that Pollena-Aroma also produces a great assortment of compositions for scenting cosmetic products, soaps, and various other household and technical products. In addition to these items, the plant manufactures perfumery raw materials, including more than one hundred products, principally synthetic basic chemicals such as benzyl acetate, methyl anthranilate, nerolin, bromelia, trichloromethylphenylcarbinyl acetate, p-tert-butylcyclohexanyl acetate, heliotropin, alpha-amylcinnamic aldehyde, cinnamic aldehyde, ethylhexyl acetate, undecalactone, salicylates, ionones, methylionones, and so on, as well as a group of resinoids like benzoe, galbanum, tolu, some isolates, e.g., citral ex litsea cubeba, absolutes, and several specialties. Pollena-Aroma's production is destined for export to West European countries as well as for its own use.

Production value of the fragrance compositions amounts to $15 million; that of the synthetic materials to about $9 million (US) (Table II).

The Pollena-Aroma plant also imports essential

Table II

Expected Production Increase—1970-1990

	1970	1975	1980	1985	1990
perfumery compositions	100	150	300	450	600
odoriferous substances	100	170	300	550	860

oils, synthetics bases, and, in some cases, finished compositions.

Poland is, however, also a producer of essential oils. This production is under the control of the Association of the Herb Industry, "Herbapol" to which some factories as well as experimental stations that conduct investigations of plant cultivation belong. Herbs are used for medicinal purposes in mixtures of herbs, galenicals, and other preparations, as well as for raw materials in the production of essential oils. Types of essential oils, and the quantity (in kg) of each, produced in Poland in the period from 1960 to 1974 are listed in Table III.

Table III

	1960	1965	1970	1974
Oil of Silver Fir	10,638	6,045	4,793	3,405
Oil of Pinus Silvestris	12,469	29,231	7,791	9,394
Oil of Peppermint	29,416	39,405	38,397	45,866
Oil of Caraway	3,745	6,740	4,190	14,940
Oil of Coriander	1,166	1,296	-	814
Oil of Sage	21	681	623	1,568
Oil of Thyme	2,707	-	178	173
Synthetic oil of Silver Fir and Pinus Silvestris	-	17,406	41,281	51,889
Oil of Carott Seed	18	361	665	136
Other *	2,301	838	960	772
Total	62,479	102,003	98,878	128,957

* Oil of Calamus, Oil of Fennel, Oil of Laurel, Oil of Angelica root, Oil of Valerian, Oil of Camomille, Oil of Sweet Marjoram and Oil of Lovage

Raw material shortages and the rapid growth of the cosmetics, perfumery, and detergent industries have made it necessary to increase production capacity and to broaden the range of products. This, in turn, has required considerable added investment and further research development in the Polish scientific centers. Research is conducted at the Institute of Food Chemistry (formerly the Institute of Synthetic Perfumes and Essential Oils) of the Technical University at Lodz as well as in the research laboratories of the Pollena-Aroma plant and at the Institute of Industrial Chemistry in Warsaw. The Institute of Food Chemistry, which I represent, also participates in the education of students in the field of perfumery technology. In this area, we have the aid of several French houses as well as scholarships provided by the French government. This is very important because most Polish consumers prefer the French type of perfume.

Recent work in the synthesis of perfumery materials

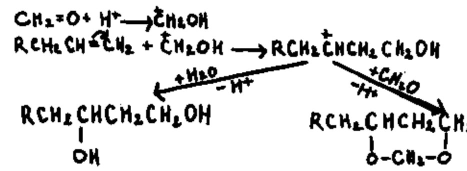
In the Institute of Food Chemistry of the Technical University in Lodz, we use the simplest technological processes, and at the same time we make use of indigenous raw materials received from the chemical industry as well as from natural sources.

We have obtained a great assortment of perfumery compounds from petrochemical products. After World War II petroleum became very important not only as a fuel, but also as a raw material of great value to the chemical industry. The n-α-olefins, being among the products easily made through the process of cracking n-paraffins obtained from the petroleum, are very valuable in organic syntheses because of their reactivity, which results from the presence of double bonds. Although the literature on the utilization of n-α-olefins in the chemical industry is extensive, there is no precise mention concerning the possibility of applying these hydrocarbons to the synthesis of fragrance compounds.

For this reason, the n-α-olefins C_7-C_{18} were the object of our investigations. Ozonolysis reaction of these hydrocarbons gave the aliphatic aldehydes C_6-C_{12} with the yield of 75%-80%.

This method is simpler and more economical than conventional means which often depend on expensive raw materials and several stages of synthesis. In addition the aldehydes obtained by this method are chemically pure to a high degree.

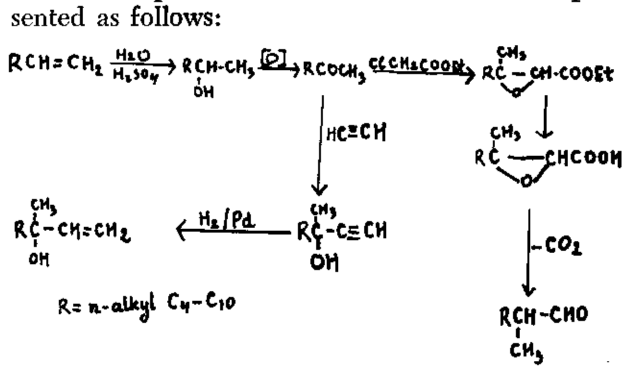
The other way of utilizing the n-α-olefins in the synthesis of odoriferous compounds consists of transforming them according to the Prins reaction in the corresponding alkyl 1,3-glycols and alkyl 1,3-dioxanes:



The yield of this reaction amounts to 70%-75%, and the molecular ratio of the compounds is 1:1.

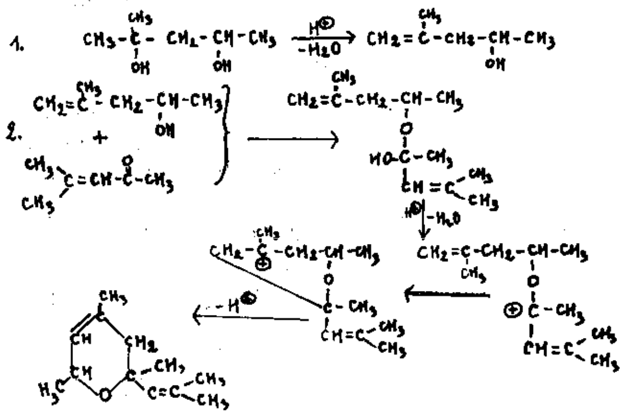
The materials obtained in this manner, alkyl 1,3-glycols and alkyl m-dioxanes, have a characteristic odor, very agreeable, with different green notes. Some of them have value for perfumery.

The other group of compounds obtained in the reaction of n-α-olefins hydration includes the secondary alcohols which have interesting odors from the perfumery standpoint. These alcohols can also be used as starting materials for the synthesis of other odoriferous products. These reactions can be represented as follows:



The cycle of effected reactions consists of the oxidation of the alcohols obtained from the corresponding ketones. Part of these are utilized for the synthesis of the methyl-n-alkylacetaldehydes according to the Darzens method; others, for the syntheses of the corresponding methyl-n-alkyl vinylcarbinols in the ethynylation reaction followed by the selective hydrogenation of acetylenic bond. Most of the compound groups have fruity odors with different floral and green notes.

In other studies in the synthesis of novel perfumery materials, we elaborated the synthesis of 2-(2′-methyl-1′-propenyl)-2,4,6-trimethyl-3-hydro-α-pyran having a structure and odor similar to rose oxide as in Bulgarian otto of rose. According to the patent literature, this compound can be obtained with a yield of 25% in the condensation reaction of 2-methyl,2,4-pentadiol with mesityl oxide in the presence of diluted sulfuric acid:



In our work the yield of this reaction, which was carried out according to the literature data, amounted to only 15%. We also found that the yield can be increased considerably, up to 70%, when diacetone alcohol is used instead of mesityl oxide and when the reaction is carried out in a homogeneous medium in the presence of an emulsifier (for example, alphenol). In addition, through this modification we eliminated one step of the reaction, the dehydration of diacetone alcohol to mesityl oxide. This method has been patented in Poland.

The nitriles are another group of compounds, some of which have become useful in perfumery, primarily because of their strong and lasting odors. Synthesis of nitriles includes certain reactions which do not always proceed smoothly and with good yield. Taking this known fact into account, we were interested in learning to what degree nitriles could be replaced by the corresponding cyanoethers in perfume compositions. For this reason, we paid special attention to the cyanoethylation of alcohols consisting of the addition of acrylonitrile to these compounds.

$$ROH + CH_2{=}CH{-}CN \longrightarrow ROCH_2CH_2{-}CN$$

Aliphatic, alicyclic, aromatic, and terpene alcohols were used as starting materials for the synthesis of these cyanoethers. Benzylammonium hydroxide (Triton B) or aqueous solution of potassium hydroxide served as catalyst. Reaction yields amounted to 50%-77%. The odoriferous properties of the synthetics produced by this reaction are presented in Table IV.

These data show that in many cases the β-oxynitriles obtained have interesting odors, sweeter than the alcohols from which they are derived.

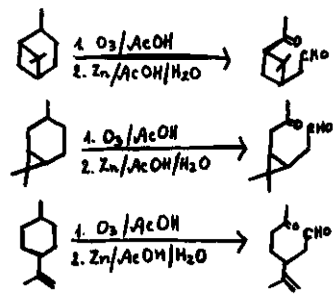
As mentioned earlier, in addition to raw materials produced by the chemical industry, raw materials derived from plants have importance in the synthesis of perfumery materials. Of great value in this respect are turpentine oil and its principal constituents, such as α-pinenes, carene-3, and limonene obtained in the process of deterpenation of citrus essential oils. Another important natural product is α-fellandren, which occurs in various eucalyptus essential oils.

Table IV

Cyanoethylation of Aliphatic Alcohols

Alcohol	Odor of the obtained β-oxynitriles
A.	
n-hexanol-1	like a wine with a note of lemon
n-heptanol-1	green with a note of fusel oil
n-octanol-1	no perfumery
n-octanol-2	like n-octanol-2 with a green note
n-nonalol-1	like n-nonalol-1 with a note of fusel oil
n-decanol-1	like n-decanol-1 with a note of ambergris
n-undecanol-1	like n-undecanol-1 and n-undecen-10-ol-1
methylisobutylcarbinol	like bergamot essential oil
B.	
fenchol	like fenchon with a green note
dihydroelgenol	like essential oil of bois de rose
isoborneol	like isoborneol but with a finer and fresher note
citronellol	like citronellol with a note of tuberose, narcissus and white lilac
dehydrolinalol	weaker than the starting alcohol
geraniol	like geraniol with a green note
C.	
3,5,5-trimethylcyclohexanol	like menthon, fenchon, and borneol
4-ethylcyclohexanol	weak, rosy with a fruit note
4-isopropylcyclohexanol	weak, fruity and flowery
3,5-dimethylcyclohexanol	fresh, musklike with a rose note
benzyl alcohol	weaker and sweeter than α-terpineol with a lilac note
β-phenylethyl alcohol	like β-phenylethyl alcohol with a musklike note

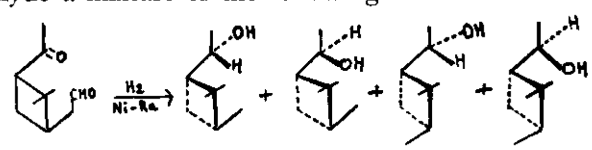
These hydrocarbons were the starting materials in the synthesis of novel perfume compounds. The reductive ozonolysis of α-pinene, carene-3, and limonene gave the corresponding keto-aldehydes.



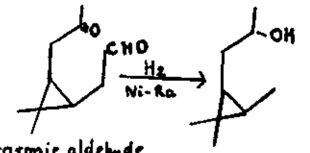
The organoleptic properties of these keto-aldehydes include 1) resinous, woody odor with a green note; 2) lime oil odor; 3) resinous odor with a weak note of fennel oil.

Taking into account the fact that isolation of α-pinene and carene-3 in the pure state from the turpentine oil is not easy because of the necessity of applying efficient distillation columns, we have also elaborated ozonolysis of turpentine oil as such. We found that the mixture of the keto-aldehydes obtained in this way, having the admixture of small quantities of by-products, results in an odor which is more agreeable and more harmonious than the individual compounds.

The keto-aldehydes also serve as starting materials for the synthesis of novel fragrance compounds. Hydrogenolysis of these compounds in the presence of Ni-Ra as catalyst gives the secondary alcohols having one atom of carbon less than the starting compounds. Thus, we obtained from pinonic aldehyde a mixture of the following isomeric alcohols:

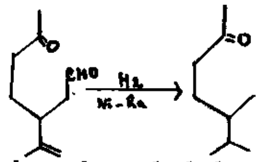


The analogous reaction in the case of hydrogenolysis of caronic aldehyde leads to 2,2,3-trimethyl-(β-hydroxypropyl)-1-cyclopropan:



caronic aldehyde

The hydrogenolysis of the aldehyde 3-isopropenyl-4-acetyl-4-n-valeric gives 2-isopropyl-5-methyl-5-hydroxy-pentan:

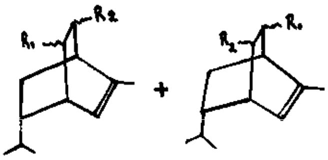


The odors of these three alcohols, although somewhat differentiated, are the linalool type, while their acetates have scents resembling lavender oil.

Hydrogenolysis of the product obtained in the ozonolysis of turpentine as such gives a mixture of compounds with an odor of the linalool type with a light note of borneol. Upon acetylation of this product, a composition with an odor similar to spike-lavender oil was obtained.

The methods of hydrogenolysis described here are patented in Poland.

Finally, I wish to introduce a novel group of fragrance compounds obtained through the Diels-Adler reaction by the 1,4 addition of certain ethylenic compounds, such as acrylonitrile, methyl acrylate, aldehyde crotonic, and acrolein to α-fellandren. These syntheses followed the conditions generally used in this type of reaction. According to expectation, a mixture of isomers in various ratios was obtained. The general course of these reactions follows.



1. R_1=-H, R_2=-CN   3. R_1=-CH_3, R_2=-CHO
2. R_1=-H, R_2=-$COOCH_3$ 4. R_1=-H, R_2=-CHO

Odoriferous properties of the compounds obtained are presented in Table V. The table indicates that the products have interesting and agreeable odors, and can, no doubt, be introduced to modern perfumery.

Table V

Odorous Properties of Products obtained in Diels-Alder Reactions

Dienophil	Odor
Acrylonitrile	woody, fruity, with a note of cedarwood and fennel oil
Methyl acrylate	peppery and woody, similar to sandalwood oil
Acroleine	strong, fresh, herbaceous
Crotonaldehyde	strong, odor of chrysanthemum and greenery predominate with a note of condiments

This, then, is the present situation in the perfumery industry of Poland, including the main investigations in the field of synthetic perfumery materials that have been made in recent years.

Acknowledgment

This paper was first presented on December 2, 1975, at the Academie d'Osmologie et de Dermologie in Paris, France.