Historical Note

Philippe Barbier and His Knowledge of Plants and Inorganic Principles in the Nineteenth Century

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Abstract

Natural principles have intrigued humans since the very beginning of history. Most of these substances entered everyday life culture by trial an error and become popular without any knowledge of their properties, constitution, and limitation. They found use as foodstuff, medicines, poisons, weapons, religious and magic rituals, dyes, arts, technology, etc. Philippe Barbier (1848-1922) (For biographical details, vide Appendix), a French chemist and pharmacist, is well known for the chemical reaction that carries his name. This fact has probably obscured the extensive work he developed about the detailed knowledge of many valuable plant and inorganic principles, among them safranines, geraniol, rhodinol, citral, limonal, and camphor. He was also the first to use organomagnesium halide reagents in organic synthesis.

Key words: Camphor, Citral, Fluorene, Geraniol, Lemon grass, Natural substances, Rhodinol, Safranin

1. INTRODUCTION

Natural principles have intrigued humans since the very beginning of history. Most of these substances entered daily life culture by trial an error and become popular without any knowledge of their properties, constitution, and limitation. They found use as foodstuff, medicines, poisons, weapons, religious and magic rituals, dyes, arts, technology, etc. Little by little their use became more refined and with the advance of science their nature, abilities and disabilities, mode of action, etc. became understood. The most significant advance occurred in the 18th and 19th centuries, particularly with the adoption of Antoine-Laurent Lavoisier (1743-1794)[1] new chemistry. Philippe

Barbier (1848-1922) is well known for the chemical reaction that carries his name. This fact has probably obscured the extensive work he developed about the detailed knowledge of many valuable plant and inorganic principles. Here we present a short description of his contribution to this important issue of human economy.

2. PLANT PRINCIPLES

2.1 Camphor

In 1892 Barbier announced that he had found a new isomer of camphor, *puleone*, in the essence of pennyroyal (*Mentha pulegium*, L.) (Barbier, 1892a). He obtained it by fractional distillation of the essence of pennyroyal, collecting

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[1] Lavoisier was the most famous French chemist of the 18th century. He revolutionized chemistry and is recognized as the father of modern chemistry. His book *Traité Élémentaire de Chimie* (Elementary Treatise of Chemistry) became the standard textbook of chemistry for many years in France and abroad. He died in the guillotine.

the fraction passing between 215° to 225 °C, and redistilling it again. Puleone was found to contain, by weight, 79.04% carbon, 10.7% hydrogen, and 10.26% oxygen, corresponding to the formula $C_{10}H_{16}O$. It was a colorless liquid, smelling strong like mint, boiling between 222° and 223 °C, and was insoluble in water and soluble in alcohol, ether, and benzene. It was dextrorotatory and had relative density 0.9482 at 0 °C. It contained a ketone group C=O, as shown by its combination with hydroxylamine to yield *puleoxime*, $C_{10}H_{16}$=NOH. Puleoxime was a colored liquid having a strong smell and decomposing when distilled at room pressure. Upon oxidation with the chromic mixture it turned into an acid crystallizing as fine silky needles, very soluble in ether, alcohol, and water, and of formula $C_7H_{12}O_4$. Barbier added that puleone did give addition products, showing that it did not contain double bonds. With phosphorus pentachloride it produced a chlorinated product of formula $C_{10}H_{15}Cl$, which upon distillation decomposed into HCl and *p*-cymene (Barbier, 1892a).

2.2 Essence of *Licari kanali*

Henri Morin[2] wrote that this essence was extracted by steam distillation from a tree growing in Guyana (Morin, 1881, 1882). It was a limpid, and slightly colored liquid, smelling like rose and citron, of relative density 0.868 at 15 °C, levorotatory, and boiling at 198 °C (755 mmHg). It was soluble in alcohol, glycerin, and ether. It was not altered by KOH and was attacked lively by bromine, iodine, nitric and sulfuric acid. Elemental analysis indicated that its composition was similar to that of camphor of Borneo: 77.77% carbon, 11.90% hydrogen, and 10.33% oxygen, corresponding to the formula $C_{20}H_{18}O_2$. Treated with fused zinc chloride it split into water and a hydrocarbon of formula $C_{20}H_{16}$, with a strong increase in temperature. This result indicated that it was an isomer of camphor of Borneo. With HCl

it generated a well-defined liquid chlorhydrate of relative density 1.069 a 16 °C and composition $C_{20}H_{16}$, 2HCl. The hydrocarbon of formula $C_{20}H_{16}$ was a colorless liquid, with a slightly aromatic smell, inert to polarized light, relative density 0.835 at 18 °C, and isomer with turpentine. Morin suggested naming it *licarene* (Morin, 1881, 1882).

Barbier decided to investigate this essence further in order to determine its constitution and chemical functionality (Barbier, 1892b). He reported that the essence he had employed boiled at 199°-200 °C, had a relative density 0.8662 at 15.4 °C, and a rotatory power $[a]_D$ = -18°21' at 15.4 °C. He named the compound $C_{10}H_{18}O$ *licareol*. He found that this compound reacted with HCl to produce a dichloride of formula $C_{10}H_{18}Cl_2$, boiling at 155°-157 °C (1039 mmHg) and relative density 1.0246 at 19.5 °C. Barbier treated the dichloride with a boiling solution of glacial acetic acid in potassium acetate, and also with acetic anhydride in a closed vessel. In both cases he obtained the acetate of a monoatomic alcohol and a hydrocarbon of formula $C_{10}H_{16}$, (which he named later as *licarene*) boiling between 177° and 178 °C. A similar process was used to prepare the methyl and ethyl esters. Barbier reported that licareol was strongly attacked by the chromic mixture and that one of the products of this oxidation was a compound of formula $C_{10}H_{16}O$, which he named *licareone*. The formation of the esters indicated clearly the alcoholic nature of licareol; the formation of the dichloride, the presence of a double bond, and the formation of licareone signaled that the alcohol was secondary (Barbier, 1892b).

Barbier reacted one mole of licareol with two of bromine and observed that no HBr was released. The product was an almost colorless viscous liquid having an elemental composition equivalent to the formula $C_{10}H_{18}Br_4O$, that is, licareol tetrabromide. Boiling this tetrabromide with silver oxide resulted in the elimination of the

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[2] A French chemist that studied the vegetable essences coming from French Guiana.

bromine and its replacement by the group OH (Barbier, 1893ac). Repeating the oxidation of licareol with larger quantities of the material resulted in the formation of a derivative containing less hydrogen, of formula $C_{10}H_{16}O$, which Barbier named *licareal*. Licareal was a colorless and slightly oily liquid, smelling like citron, boiling at 118°-120 °C (20 mmHg), and decomposing when boiled at atmospheric pressure. Licareal did not act on polarized liquid and reacted with hydroxylamine forming an oily oxime of formula $C_{18}H_{17}NO$. This oxime, boiled with acetic acid, lost one molecule of water and became *licaric nitrile*, $C_{10}H_{15}N$. The reaction of licaric nitrile with a concentrated solution of KOH resulted in the release of ammonia and formation of the potassium salt of a new acid, *licaric acid*, of formula $C_{10}H_{16}O_2$. The results of these and other reactions led Barbier to change his opinion: he now declared that licareol was a *primary alcohol* having the formula C_9H_{15}-CH_2OH (Barbier, 1893a).

A following publication was devoted to licarene, $C_{10}H_{16}$, the new hydrocarbon previously discovered (Barbier, 1892b, 1893b). This was a mobile liquid, of pleasant odor, boiling between 176°-178 °C (760 mmHg), relative density 0.8445 at 0 °C, and rotatory power $[a]_D = 7°51'$ at 20 °C. It combined with bromine producing a mixture of two tetrabromides, one liquid and the other solid. The solid one melted at 103°-104 °C and oxidized by means of the chromic mixture it produced terpenic and acetic acid. Licarene reacted with HCl yielding a dichloride of formula $C_{10}H_{18}Cl_2$, optically inactive, boiling at about 155 °C (39 mmHg) and relative density 1.0466 at 0 °C. These and other properties indicated that licarene belonged to the category of limonenes (Barbier, 1893b).

Barbier published two additional papers related to licareol, one giving it possible constitution (Barbier, 1893c) and the other about the formation of an acetic ester when reacting with acetic anhydride in a closed vessel (Barbier, 1893d). The ester, of formula C_9H_{15}-$CH_2OC_2H_2O$, was a colorless liquid, insoluble in water, boiling at 135 °C (21 mmHg), and presenting a low optical activity. This ester was rapidly saponified by alcoholic KOH, liberating a new alcohol, that Barbier named *licarhodol*. Licarhodol boiled a 122 °C (19 mmHg) and its elemental composition corresponded to the formula $C_{10}H_{14}O$, in other words, the same as licareol but possessing different physical properties (Barbier, 1893d).

In his last paper on the subject, Barbier proved that the alcohol contained in the essence of coriander, named *coriandrol*, was the dextrorotatory modification of licareol (Barbier, 1893e).

Barbier and Louis Bouveault (1864-1909)[3] added more information about the constitution of licareol (Barbier and Bouveault, 1894e). As mentioned above, Barbier had already stated that licareol was a levorotatory primary alcohol containing two double bonds and capable of transforming into a stable dextrorotatory stereoisomer under the influence of acetic anhydride. Barbier and Bouveault studied the oxidation of licareol in order to obtain additional information about the constitution of this alcohol. For this purpose they treated licareol with the chromic mixture in a refrigerated flask. The reaction was very strong and generated, among other products, acetone, C_2H_6O, characterized by its odor, boiling point, and the formation of iodoform, unchanged licareol, licareal or licarhodal, boiling at 111°-112 °C (13 mmHg), a methyl heptenone, $C_8H_{14}O$, a mixture of acetic and

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[3] French chemist and physician who studied in detail the synthesis of a large number of new compounds, among them, *b*-ketone nitriles, primary alcohols, fatty acids, etc. His most important contribution is the Bouveault synthesis of aldehydes. He studied in detail the separation and properties of numerous plant extracts, among them, rhodinol, rhodinal, lemon grass, lemonals, citronell, etc.

formic acids, and a methyl heptenone carbonic acid, $C_8H_{13}OCOOH$. Using an excess of chromic mixture led to formation of a mixture of acetic and formic acids not containing higher fatty acids, and terebic acid, $C_7H_{10}O_4$ (Barbier and Bouveault, 1894e). Each of the products of these reactions was reacted with a variety of reagents in order to verify their identity. As a result, Barbier and Bouveault concluded that licareol had the following structure corresponding to an active alcohol (Barbier and Bouveault, 1894e).
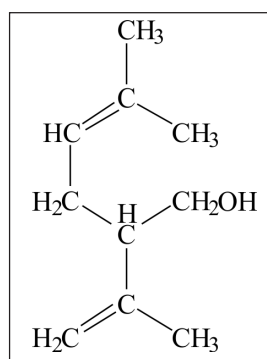

Fig. 1. Licareol

2.3 Geraniol

Barbier (alone or in collaboration with Bouveault) also studied the essence of geraniol, $C_{10}H_{18}O$, extracted from the plant camel grass (*Andropogon Schoenanthus*) by vacuum distillation (Barbier, 1893f, Barbier and Bouveault, 1894d). He described it as a liquid boiling at 126°-127 °C (16 mmHg) and containing traces of a sesquiterpene that increased its density and gave it optical activity. Friedrich Wilhelm Semmel had determined that this essence was an inactive primary alcohol containing two double bonds, which yielded valeric acid when strongly oxidized (Semmel, 1890). Barbier reacted geraniol with acetic acid in a closed vessel at 150 °C and found that acetic ester, $C_{10}H_{17}OC_2H_3O$, was the only product. This purified compound was a colorless liquid, of agreeable odor, boiling at 126°-127 °C (16 mmHg), relative density 0.9012 at 0 °C, and slightly levorotatory. According to Barbier, Gustave Bouchardat (1842-1918)[4] had found in the essence of lavender a linalol, which he considered to be identical with licareol (Bouchardat, 1893). A comparison of the physical properties of both compounds, licareol and geraniol, indicated that the linalol of lavender was a unstable stereoisomer of geraniol (Barbier, 1893f, Barbier and Bouveault, 1894d).

2.4 Rhodinol

Barbier wrote that several chemists had investigated *rhodinol*, $C_{10}H_{18}O$, the chemical principle present in the liquid part of the essence of roses, and shown it was an active primary alcohol containing two double bonds, and yielding valeric acid upon oxidation (Barbier, 1893g). The properties of rhodinol seemed to indicate it was an isomer of licareol and geraniol. Barbier studied the reaction of rhodinol with gaseous HCl and with acetic anhydride and verified that this assumption was correct. The rhodinol he used was an oily liquid, boiling without decomposition at 126.5 °C (16 mmHg), relative density 0.8956 at 0 °C, and rotatory power $[a]_D$ = -2°37' at 25 °C. Upon reaction with dry HCl it lost water and yielded a liquid dichloride boiling at 147 °C (18 mmHg) and relative density 1.051 at 0 °C. Barbier wrote that HCl acted like a dehydrating agent, closing the chain and giving a cyclic arrangement of dipentene dichloride. The latter, treated with a boiling solution of potassium acetate in acetic acid, produced dipentene, a result indicating that the constitution of rhodinol corresponded to the structure (Barbier, 1893g):

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[4] French pharmacist and physician considered as the founder of diabetology. Carried a large number of researches on environment protection, public and work hygiene, metabolic disorders, fertilizers, plant physiology, food chemistry, organic chemistry, etc.
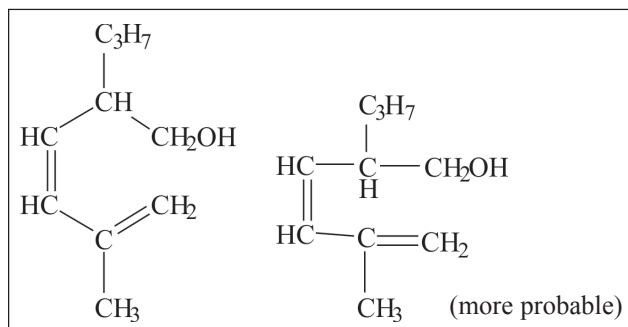
Fig. 2. Rhodinol

Barbier and Bouveault carried on additional experiments in order to determine the constitution of rhodinol (Barbier and Bouveault, 1896a). For this purpose they oxidized the alcohol with the chromic mixture and obtained (a) a volatile product boiling at 90 °C (10 mmHg) smelling strongly like mint and having formula $C_{10}H_{18}O$. This product was an aldehyde, which they named *rhodinal*, (b) an oily monobasic acid having a strong disagreeable odor, boiling at 147 °C (10 mmHg), formula $C_{10}H_{18}O_2$, and which they named *rhodinic acid*. This acid fixed one molecule of brome and was identical with a product described previously during the study of the oxidation of the rhodinol of the essence of pelargonium, to which they had erroneously assigned the formula $C_{10}H_{16}O$; (c) a neutral oil boiling at 190 °C (10 mmHg), and crystallizing as fine silky needles, very soluble in neutral solvents (except petroleum ether), which melted at 92 °C; and (d) more oxidized products, such as dimethyl acetone and a dibasic crystalline acid, of formula $C_7H_{12}O_4$, soluble in water, melting at 95 °C, and identical to β-methyladipic acid. The same results were obtaining by oxidizing the rhodinol from the essence of roses. These results showed that the rhodinol obtained from the essences of pelargonium and roses was one and the same. According to Barbier and Bouveault, the formation of rhodinal, of rhodinic acid, and of rhodinyl rhodinate, proved that rhodinol was a primary alcohol having an ethylene bond (Barbier and Bouveault, 1896a).

Barbier and Bouveault also proved that rhodinal was easily transformed into menthone (Barbier and Bouveault, 1896b).

2.5 Acyclic Isomers of Borneol

Barbier wrote that certain natural essences such as those of Licari kanali, coriander, linaloe, geranium and roses, were almost exclusively composed of chemical substances of formula $C_{10}H_{18}O$ and having alcohol properties. He then proceeded to summarize all the results he had obtained for licareol, rhodinol, and geraniol, and added more information about linalol and coriandrol. Licarhodol, the stereoisomer of licareol, was obtained starting from the acetic derivative of the latter, $C_{10}H_{17}OC_2H_3O$ (Barbier, 1893h).

The essence of coriander contained an alcohol, $C_{10}H_{18}O$, known as coriandrol, which could be easily separated by repeated fractional distillation under vacuum. It was a colorless liquid, smelling like the coriander seeds, boiling at 93^0-94 °C (15.5 mmHg), relative density 0.8820 at 0 °C, and rotatory power $[\alpha]_D = 15^021'$ at 20 °C. The chromic mixture converted it into an aldehyde named *coriandral*, of formula $C_{10}H_{16}O$, boiling at 180^0-182 °C (15 mmHg), and relative density 0.9089 at 0 °C. The aldehyde reacted with sodium bisulfite producing a crystalline derivative, and with hydroxylamine a liquid oxime of formula $C_{10}H_{17}NO$, and having the same physical and chemical properties of licareal. Coriandral added bromine to yield a liquid tetrabromide, $C_{10}H_{18}Br_4O$. Coriandrol reacted with HCl gas to yield a liquid dichloride, $C_{10}H_{18}Cl_2$, boiling at 133^0-135 °C (17 mmHg), relative density 1.0445 at 0 °C, and having no optical activity. Coriandrol, heated in a closed vessel at 150 °C with acetic anhydride, lost water and produced a dextrorotatory limonene. This limonene had the same physical and chemical properties as the limonene obtained from licareol under the same circumstances. The acetic ester of coriandrol was

saponified by KOH producing *levorotatory licarhodol*. All these results pointed out to the analogy between coriandrol and licareol. They showed that coriandrol was an unstable stereoisomer, capable of changing into levorotatory licarhodol, which was the stable form (Barbier, 1893h).

Barbier summarized these findings as follows: (a) the licareol obtained from the essence of Licari kanali had two stereoisomers; the levorotatory was unstable and the dextrorotatory stable, and (b) the licareol obtained from the essence of coriander had two stereoisomers; the levorotatory was stable and the dextrorotatory unstable (Barbier, 1893h).

Linalol was obtained from the linaloes by repeated fractional distillation under vacuum. It usually appeared as an oily liquid boiling at 98°-100 °C (14 mmHg), relative density 0.8869 at 0 °C, rotatory power $[a]_D$ = -11°55' at 23 °C, and having a composition corresponding to the formula $C_{10}H_{18}O$. Upon oxidation it yielded an aldehyde of formula $C_{10}H_{16}O$ and an acid of formula $C_{10}H_{16}O_2$, together with substantial amounts of valeric acid. With bromine it produced a tetrabromide, $C_{10}H_{18}Br_4O$, with gaseous HCl a liquid dichloride, $C_{10}H_{18}Cl_2$, able to regenerate a tetratomic terpene, $C_{10}H_{16}$, by loss of HCl. All these results suggested that the constitution of linalol was given by the following structure exactly identical to that of rhodinol, although with different properties. Acetic anhydride transformed
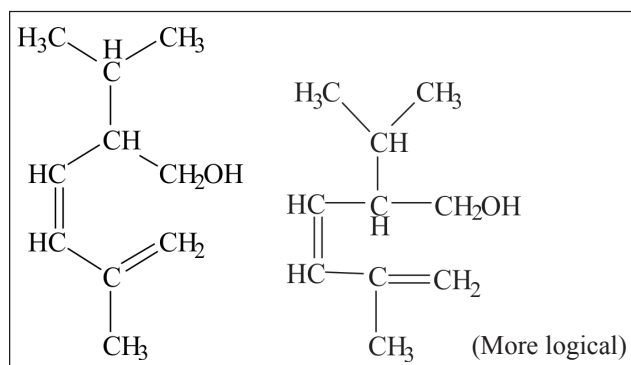

Fig. 3. Linalol

levorotatory linalol into dextrorotatory rhodinol and racemic rhodinol (identical with geraniol) (Barbier, 1893h).

Barbier and Bouveault carried on a complete analysis of the essence of Linalöe and found that it contained 1/1000 of a diatomic terpene and 1/1000 of a tetratomic terpene, 1/1000 of methylheptenone, 1/100 of licareol, 1/100 of licarhodol, and /100 of sesquiterpene (Barbier and Bouveault, 1895b).

2.6 Lemonol

Barbier (1898a) reported that he had prepared a new tertiary alcohol by the reaction between lemonol and alcoholic KOH. This alcohol was particularly interesting because it was a primary alcohol and was present in small quantities in certain natural essences (Barbier, 1898a). Its preparation involved heating in a bronze vessel a mixture of 200 g of lemonol and 100 g of KOH dissolved in a very small amount of alcohol, for 8 hours at 150 °C. The new alcohol was precipitated from the product by water, washed with a diluted solution of acetic acid, dried, and then separated by fractional distillation under vacuum. It was a colorless liquid, of agreeable aromatic odor, boiling at 70 °C (10mm Hg), and containing by weight 76.08% carbon, 12.60% hydrogen, and 11.32% oxygen. It fixed one mole of bromine and heated with acetic anhydride and sodium acetate it yielded an aromatic ester boiling at 84°-86 °C (11 mmHg). These results indicated that the new body was an unsaturated alcohol of formula $C_9H_{18}O$, differing by one carbon atom from the primitive alcohol. Barbier determined its structure by preparing the semicarbazone, and its oxidation by means of the chromic mixture:

$$CH_3\,HC\,HCH\,H(CH2)_2\,HC(OH)\,HCH_3$$
$$\quad\quad |\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad CH_3\quad\quad\quad\quad\quad CH_3$$
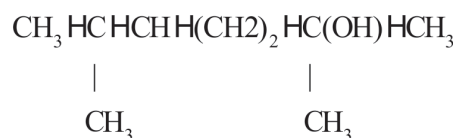
That is, dimethyl-2,6-heptene-2-ol-6 (Barbier, 1898a).

2.7 Lemonal

Barbier distilled under vacuum the essence of lemon verbena (*Lippia critiodora*) and obtained 65 to 70% of a liquid smelling like citron, inactive on polarized light, and boiling at 106°-108 °C under 10 mmHg (Barbier, 1899c). Elemental analysis indicated that it was an aldehyde of formula $C_{10}H_{16}O$. Upon oxidation it yielded the same products as lemonal and upon boiling with potassium carbonate it also split into 2,2,6-methyl heptenone and acetaldehyde. Treated with hydroxylamine it yielded an oxime boiling at 119°-120 °C (10 mmHg) and a small amount of an isomeric oxime boiling at 143°-145 °C (10 mmHg), identical to lemonal oxime. The main oxime reacted with acetic anhydride yielding a nitrile boiling at 114°-115 °C (10 mmHg), of formula $C_{19}H_{15}N$. Under the same conditions, the second oxime also yielded a nitrile. Treating the lemonal of the essence of lemon verbena, boiling at 106°-108 °C (10 mmHg), with an alcoholic solution of semicarbazide hydrochloride and sodium carbonate, yielded a mixture of semicarbazones, containing mostly a modification melting at 171 °C. These results put in doubt the existence of two isomeric lemonals (Barbier, 1899c).

2.8 Lemon grass

In 1890 Frank Despard Dodge[5] reported that lemon grass (*Andropogon citratus*) contained an aldehyde of formula $C_{10}H_{16}O$, which he named *citriodoric aldehyde* (Dodge, 1890). This aldehyde was afterwards named *citral* by Ferdinand Tiemann (1848-1899)[6] and Semmel (Tiemann and Semmel, 1893). Barbier and Bouveault decided to study this essence in more detail. For this purpose they subjected it to a series of fractional distillations under vacuum and separated three fractions boiling at 12 mmHg: (1) 65-77 °C, (2)

110-115 °C, constituting the citriodoric aldehyde, and (3) a viscous brown liquid that was not inspected further (Barbier and Bouveault, 1894b). The remaining portion was further distilled at room pressure and found to boil completely in the range 170° to 175 °C. Further inspection showed that it contained a terpene and an unsaturated acetone, which reacted easily with sodium bisulfite. The latter was separated and decomposed with sodium carbonate. The regenerated acetone was dried by distillation in the presence of acetic anhydride. It had a penetrating smell, boiled at 169°-170 °C, and contained, by weight, 79.06% carbon, 11.12% hydrogen, and 9.82% oxygen, corresponding to the formula $C_8H_{14}O$. Its reaction with sodium hypobromite and potassium iodide indicated that it contained the group $-CO-CH_3$. Further chemical reactions led to assume that its constitution was

$$CH_3\,HCHCHH(CH2)_2\,HCOHCH_3$$
$$|$$
$$CH_3$$
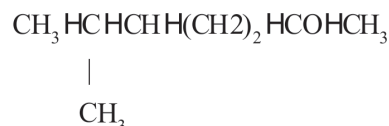
that is, it was methyl-2-heptene-2-one-6, different in properties from the one prepared previously from the reaction between isovaleric aldehyde and acetone (Barbier and Bouveault, 1894a). Methyl-2-heptene-2-one-6 produced an oxime boiling at 111 °C (10 mmHg), which combined energetically with acetic anhydride to yield an acetyl derivative boiling with decomposition at about 125 °C (Barbier and Bouveault, 1894b).

Barbier and Bouveault assumed that the natural methylheptenone they had described before (Barbier and Bouveault, 1894b) originated from the oxidation of citriodoric aldehyde, and that these two bodies had an analogue constitution (Barbier and Bouveault, 1894c). In order to test this hypothesis they oxidized their aldehyde with

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5 American chemist. Determined the composition of camphene, isolated citronellol and distinguished it from citronnellal, purified many essential oils, etc.

6 German chemist, co-discoverer of the Reimer-Tiemann reaction used for the ortho formylation of phenols.

a mixture of sodium dichromate and sulfuric acid and obtained a mixture of volatile and non-volatile acids. The latter were removed with ether, followed by purification by means of evaporation, treatment with sodium carbonate, and transformation into the calcium salt. The acid present was identified as methylheptenone carbonic acid, $C_8H_{13}O.COOH$. Barbier and Bouveault believed that the latter was identical with the oily acid obtained by Tiemann and Semmel, by distillation of their methylheptenone (Barbier and Bouveault, 1894c).

In a following work they submitted the main portion obtained by distillation of lemon grass to further distillation under vacuum (10 mm Hg) and by this they split it into two fractions, one boiling between 107° and 110 °C and the other, between 110° and 112 °C (Barbier and Bouveault, 1895c). The first fraction formed a semicarbazone of formula $C_{11}H_{19}N_2O$, little soluble in cold or boiling alcohol. Barbier and Bouveault obtained from the semicarbazone of the second fraction, three different crystalline products: (1) one crystallizing as white plates, little soluble in cold or boiling alcohol, insoluble in water and in boiling ether, and melting at 117 °C, without decomposition; (2) another crystallizing as needles, very soluble in hot alcohol, little soluble in boiling ether, insoluble in cold ether, and melting at 160 °C, without decomposition; and (3) a combination precipitating from alcohol at 50 °C as white needles, very soluble in cold and boiling alcohol, soluble in boiling ether, little in boiling water, and melting at 135 °C, without decomposition. These three semicarbazones were found to be isomeric and having the formula $C_{10}H_{16}$=N-NH-CO-NH$_2$. According to Barbier and Bouveault, the essence of lemon grass did not contain an aldehyde of formula $C_{10}H_{18}O$ because no additional semicarbazone was formed. In addition, the stereoisomerism was not due to the nitrogen (Barbier and Bouveault, 1895c).

In 1896 Barbier and Bouveault announced that they had succeeded in synthesizing natural methylheptenone by boiling a mixture of amylene dibromide with an excess of a solution of sodium acetylacetone in ether. The resulting isoamenyl-acetyl acetone

$$CH_3 \qquad\qquad CO\text{-}CH_3$$
$$| \qquad\qquad\quad |$$
$$CH_3\,HC\,HCH\,HCH_2\,HCH\,HCO\,HCH3$$
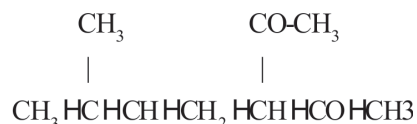
a colorless oil of sweet taste, boiling at 112°-115 °C (10 mmHg), which when reacted with a concentrated solution of NaOH and then heated, released the methylheptenone. The latter was separated by steam distillation. The purified product boiled at 1700-172 0C, the same as the natural product (Barbier and Bouveault, 1896d).

2.9 Pelargonium

According to Barbier and Bouveault, not much was known about this essence. Julius Bertram and Edouard Gildemeister had recently claimed it contained three isomers, lemonol (geraniol) of the essence of *Andropogon Schoenanthus*, the alcohol $C_{10}H_{18}O$ of the essence of pelargonium, and rhodinol of the essence of roses (Bertram and Gildemeister, 1894). The first results obtained by Barbier and Bouveault, indicated that this assumption was mistaken (Barbier and Bouveault, 1894f). Barbier and Bouveault distilled under vacuum the crude essence of pelargonium and reported that the main fraction (75%) passed in the temperature range 90°-115 °C. The crude essence was first saponified with alcoholic KOH so that the alkaline solution contained the acids in the state of esters. The distillation of this solution under vacuum produced a fraction of 5% passing below 80 °C, another of 12.5% passing between 80⁰ and 100 °C, and a third fraction of 75% distilling between 115° and 116 ⁰C. Barbier and Bouveault examined in more detail the last two (Barbier and Bouveault, 1894f).

Their results indicated that they had the same composition, corresponding to $C_{10}H_{18}O$. The fraction boiling between 115° and 116 °C had a

relative density of 0.8866 at 0 °C and a rotatory power of -12°28' (thickness 20 cm). Barbier and Bouveault named it, temporarily, *rhodinol of pelargonium*. The lower boiling fraction, 80^0-100 °C was very similar to licareol, as shown by its reaction with acetic anhydride, which yielded an hydrocarbon boiling at 60° to 80 °C under vacuum, and an acetone boiling between 90° to 95 °C. The latter was found to be a mixture of two acetones, one, saturated, of formula $C_{10}H_{18}O$ and isomeric with menthone, and another, unsaturated, of formula $C_{10}H_{16}O$. Barbier and Bouveault added that they had separated from the saponified crude essence several acids (i.e. acetic, isobutyric, isovaleric, tiglic, etc.). This preliminary results showed that the essence of pelargonium contained at least six different substances, of which rhodinol of pelargonium was the dominant one (Barbier and Bouveault, 1894f).

Barbier and Bouveault found that the principal portion of the essence of pelargonium was an alcohol, as shown by its easy conversion into its acetic ester. This ester of pleasant smell boiled at 120 °C (10 mmHg) and had a relative density of 0.9158 at 0 °C. The rhodinol of pelargonium was a primary alcohol having one double bond, as shown by its oxidation to an aldehyde of composition $C_{10}H_{16}O$, boiling 105° to 108 °C. It oxime was an oily liquid boiling between 140° to 150 °C that reacted with acetic anhydride producing a nitrile boiling 112° to 113 °C (11 mmHg). A stronger oxidation of the alcohol gave considerable amounts of dimethyl ketone. Barbier and Bouveault added that rhodinol of pelargonium reacted with potassium bisulfite to yield a viscous liquid, having a very higher boiling point, probably composed of oxides, and an extremely small amount of an unknown hydro-carbon (Barbier and Bouveault, 1894g).

2.10 Citronella

In 1889 Dodge announced the discovery of the aldehyde $C_{10}H_{18}O$ in the essence of citronella (*Andropogon nardus*); a product identical with the citronellol sold in Germany (Dodge, 1889). In 1896 Barbier and Bouveault proved that citronella was different from rhodinal, as shown by the following formulas (Barbier and Bouveault, 1896c):
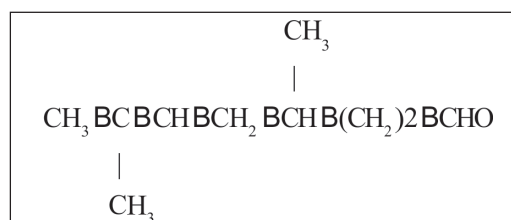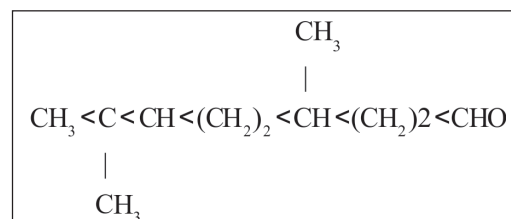
Fig. 4. Rhodinal

Fig. 5. Citronella

2.11 Coumarin

Barbier wrote that in 1820 Nicolas-Jean-Baptiste-Gaston Guibourt (1790-1867)[7] had discovered coumarin in the seeds of Tonka (*Dipterix odorata*) (Guibourt, 1820) and that afterwards it was found in a variety of other seeds and flowers (Barbier, 1879). Z. Delalande was the first to analyze it and assign the formula $C_{18}H_7O_4$ (Delalande, 1839). In 1868 William Henry Perkin (1838-1907)[8] succeed in synthesizing coumarin by reacting sodium salicylate and acetic anhydride. He reported that the sodium acetosalicylate formed crystallized as fine needles, melting at 37 °C and boiling with decomposition at 253 °C (Perkin, 1868). Tiemann and Hermann Herzfeld confirmed Perkin's findings and claimed that coumarin was

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[7] French pharmacist who studied the oxides, sulfides, and other compounds of mercury, arsenic and its compounds, a large number of natural products, among them turpentine, starch, astringent juices, and musk. Also established the norm to express the power of pepsin.

[8] English chemist, fellow of the Royal Society, and a student of Adolf von Baeyer. Known for his accidental discovery of purple mauve (the first aniline dye).
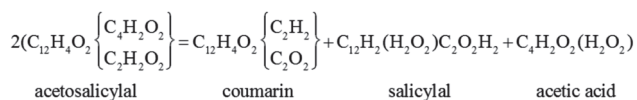
the anhydride of coumaric acid and had a constitution analogue to that of lactide, the anhydride of lactic acid (Tiemann and Herzfeld, 1877). Barbier wrote that the purpose of his thesis was to show that there was not relation between coumarin and lactide, to demonstrate that the formation of coumarin from salicylaldehyde was a very simple reaction, and to describe some features of coumarin and its relation with coumaric acid (Barbier, 1879).

Barbier carried on his experiments using coumarin extracted from Tonka seeds. This substance was present in the cotyledons of the seeds, together with a non volatile oil. The seeds were pulverized finely and completely extracted with warm alcohol. Evaporation of the alcoholic solution left a deposit of impure coumarin, which was purified by recrystallization from alcohol in the presence of animal black. The resulting coumarin crystals melted at 67 °C. The claim that coumarin was an anhydride was tested by heating it with water in a closed vessel, for 5 hours at 180 °C. No hydrolysis took place and no coumaric acid was detected. Under the same conditions lactide was completely converted into ordinary lactic acid. In an additional experiment coumarin was heated in a closed flask with an alcoholic solution of ammonia, for 4 hours at 180 °C. No change was observed. Under the same conditions lactide was completely transformed into lactamide. All these results indicated clearly that coumarin was not an anhydride (Barbier, 1879).

Barbier carefully repeated the synthesis method employed by Perkin and was unable to obtain the crystals reported by Perkin. Every time the result was a non-crystallizable and slightly colored yellow liquid. Upon distillation he separated three fractions: (1) between 110° and 180 °C, a mixture of acetic acid and salicylal; (2) between 180° and 220 °C, a mixture salicylal pure; and (3) towards 285° and 290 °C, a solid material

identified as coumarin by its melting point, its crystalline form and its odor (Barbier, 1879).

According to Barbier this reaction took place according to the following scheme:

$$2(C_{12}H_4O_2)\begin{Bmatrix}C_4H_2O_2\\C_2H_2O_2\end{Bmatrix} = C_{12}H_4O_2\begin{Bmatrix}C_2H_2\\C_2O_2\end{Bmatrix} + C_{12}H_2(H_2O_2)C_2O_2H_2 + C_4H_2O_2(H_2O_2)$$

$$\quad\text{acetosalicylal}\qquad\qquad\text{coumarin}\qquad\quad\text{salicylal}\qquad\quad\text{acetic acid}$$

He wrote that he had been able to isolate all the compounds appearing in this reaction, proving that it was the correct mechanism. He believed that it also explained the results obtained by Perkin in his first experience. The ether employed by Perkin (aqueous of alcoholic) retained at the same time the acetosalicylal and sodium acetate, which under the influence of heat reacted to yield coumarin. It also explained the results obtained when employing a mixture of acetic anhydride and sodium acetate, which yielded coumarin by its action on salicylal. It generated first acetosalicylal, which was then dehydrated by the sodium acetate (Barbier, 1879).

According to Barbier, the dehydration reaction that generated coumarin was interesting because of the two functions that characterized acetosalicylal. This compound was not an aldehyde and not a phenol because it did not combine with sodium sulfite and did not generate esters by the action of acid anhydrides. If the reaction was carried on with a *mixture* of anhydride and sodium acetate, the only product was coumaric acid without traces of coumarin (Barbier, 1879)

As mentioned before, this work on coumarin earned Barbier the title pharmacist of first class.

3. OTHER PRINCIPLES AND RESINS

3.1 Fluorene and derivatives

In 1867 Marcelin Berthelot (1827-1907)[9] announced the discovery of *fluorene*, a new

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[9]　Marcellin Berthelot, probably the most important and prolific French chemist of the 19th century. Formulated the Thomson-Berthelot principle of thermochemistry. Synthesized formic acid, methane, acetylene, and benzene.

crystalline hydrocarbon contained in raw anthracene and in coal tar (Berthelot, 1867). Berthelot obtained the fluorene by fractional distillation of raw anthracene, collecting the fraction passing between 300° and 310°C and purifying it with alcohol. When using coal tar, the anthracene and naphthalene were first wrung out and the remaining tar distilled. The fraction passing between 300° and 350 °C was redistilled, and the fraction passing between 300° and 340 °C separated and left to cool. The resulting precipitate was dried repeatedly between absorbing paper until all the attached liquid had been eliminated. The dry material was distilled and the fraction passing between 300° and 305°C separated and recrystallized from boiling alcohol. The resulting substance was a white soft solid, melting at 112 °C, quite fluorescent, and accompanied by an oxygenated impurity. The fluorene was separated by distillation, collecting the fraction passing at 300 °C and purifying it by crystallization from alcohol. The purified fluorene appeared as white flakes, presenting a violet fluorescence, a penetrating sweet smell, melting at 113 °C and boiling at 305 °C. These last two temperatures made it substantially different from all the known hydrocarbons. Berthelot described the chemical reactions with a variety of reagents (i.e. sulfuric and nitric acids, iodine, bromine, potassium, and sodium) (Berthelot, 1867).

In his first work on the subject, Barbier prepared fluorene by a slightly modified procedure: he crystallized it from a mixture of alcohol and benzene instead of alcohol alone. In this manner he was able to eliminate a small amount of acenaphthene that was present in the mother liquor (Barbier, 1873). Fluorene was very soluble in ether, benzene, carbon disulfide, and hot alcohol, and little soluble in cold alcohol; its violet fluorescence disappeared readily under the action of sunlight. Barbier used several procedures

to determine that the composition and corresponding formula of fluorene was $C_{26}H_{10}$ (today we know that the correct formula is $C_{13}H_{10}$)[10] : (a) by analysis of its picrate, (b) the complete analysis of a bromine derivative, and (c) by elemental analysis of the compound. He reported that the picrate crystallized as red needles, melting at 80°-82 °C, and was split by ammonia into its components, fluorene and ammonium picrate. Barbier prepared and described the properties of the following bromine derivatives: fluorene di, tri, and tetrabrominated, $C_{28}H_8Br_2$, $C_{28}H_7Br_3$, and $C_{28}H_6Br_4$, and monobrominated fluorene bromide, $C_{28}H_9Br_3$. He reported that fluorene was lively attacked by bromine with release of HBr. The resulting product was a viscous mass, highly colored and containing a mixture of several bromine compounds. The dibrominated compound, $C_{26}H_8Br_2$, melted a 166°-167 °C, crystallized as clinorhombic crystals containing, by weight, 49.1% bromine, and yielding upon heating to red, a hydrocarbon having the odor and aspect of diphenyl. These results seemed to suggest that fluorene had the constitution of a diphenylmethylene, probably $C_{24}H_8(C_2H_2[-]) = C_{26}H_{10}$, that is, diphenyl in which H_2 had been replaced by methylene C_2H_2. Elemental analysis of fluorene indicated that it contained, by weight, 93.6% carbon and 6.4% hydrogen. Fluorene was attacked strongly by fuming nitric acid producing several nitrated compounds, among them mono and dinitrated fluorene, $C_{26}H_9(NO_4)$ and $C_{26}H_8(NO_4)_2$. Barbier also reported that fluorene was hardly attacked by oxidants (i.e. a solution of potassium dichromate in diluted sulfuric acid or crystalline chromic acid); the main products were fluorenoquinone and diphenyl-carbonyl, accompanied by CO_2, formic, oxalic, and phthalic acids (Barbier, 1873, 1876).

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[10] Note must be taken that Barbier was using the old values of the atomic masses, i.e. C = 6, O = 8, hydrogen monoatomic, and water = OH.

In a following publication (Barbier, 1874c) Barbier reported additional experimental evidence that justified his assumption that fluorene had the constitution of a diphenylmethylene: (a) since fluorene was an incomplete hydrocarbon of order one, it had to yield with bromine an addition derivative. The result of the pertinent experiment was the compound $C_{26}H_9Br_3 = C_{24}H_7Br$ (C_2H_2 [Br_2]), that is, a monobrominated bromide, which appeared as fine yellow silvery needles, little stable. Heat and alcoholic KOH eliminated HBr leaving the dibrominated fluorene, $C_{26}H_9Br_3 = C_{26}H_8Br_2 + HBr$, melting at 166°-167 °C; (b) fluorene was oxidized by the chromic mixture into many derivatives, among them, a yellow white crystalline compound, melting about 270 °C, which Barbier believed was the quinone $C_{26}H_8O_4$; another crystalline compound, melting between 81° and 82 °C, which Barbier identified as diphenylene-carbonyl, identical with the diphenylacetone of Rudolph Fittig (1835-1910)[11] and E. Ostermayer (Fittig and Ostermayer, 1872).

Barbier tried unsuccessfully to synthesize fluorene starting from hydrocarbons of formula $C_{26}H_{12}$ (for example, diphenylmethane and phenyltoluene) (Barbier, 1874a). Heating diphenylmethane in a close tube resulted in the formation of solid phase of anthracene and a liquid one of a mixture of benzene and toluene, with no traces of fluorene. Using phenyltoluene and the same procedure generated a mixture of benzene and toluene, without traces of anthracene. The reduction of benzophenone with zinc powder also failed to produce fluorene (Barbier, 1874a).

Barbier stated that all the oxidized derivatives he had prepared from fluorene behaved in exactly the same manner in all the reactions he had tested. Both of the above products were able to fix the elements of water to yield a monobasic acid. Hence the reaction that yielded the compound $C_{26}H_8O_2$ had to be the following (Barbier, 1874b):

$$C_{24}H_8 (C_2H_2[-]) + O_4 = C_{24}H_8(C_2O_2[-]) + H_2O_2$$
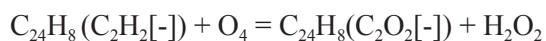
This equation showed that diphenylformic acid, $C_{24}H_8(C_2H_2O_4)$ and diphenylene-carbonyl, $C_{24}H_8(C_2O_2)$ derived directly from fluorene, making this hydrocarbon the starting point of a series of new compounds, comparable to that of propylene, with an asymmetric composition, for example a fluorenic alcohol of formula $C_{28}H_{10}O_2$, analog to allyl alcohol. Barbier obtained this compound by hydrogenating diphenyl-carbonyl (Barbier, 1874b):

$$C_{24}H_8(C_2O_2[-]) + H_2 = C_{24}H_8(C_2H_2O_2)$$
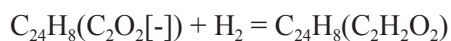
In a following publication Barbier provided detailed information about the synthesis of fluorenic alcohol (Barbier, 1875). This alcohol was prepared by reacting an alcoholic solution of diphenylene carbonyl with sodium amalgam. The product was washed and dried and then purified by precipitation from a solution in boiling benzene. Elemental analysis of the purified alcohol indicated that it contained, by weight, 85.4% carbon, 5.5% hydrogen, and 9.1% oxygen, corresponding to the formula $C_{26}H_8(H_2O_2)$. The alcohol appeared as white hard hexagonal plates, very soluble in benzene, melting at 153 °C, and oxidized by chromic acid again into diphenyl carbonyl. Heated to a temperature above the melting point transformed it into a resinous substance melting about 290 °C, which proved to be fluorenic ether, $C_{26}H_5(C_{26}H_{10}O_2)$; heated with anhydrous acetic acid for several hours at 100 °C transformed it into fluorenacetic ether, $C_{26}H_8(C_4H_4O_4)$, a crystalline material melting at 75 °C:

$$C_{26}H_8(H_2O_2) + C_4H_4O_4 = C_{26}H_8(C_4H_4O_4) + H_2O_2$$
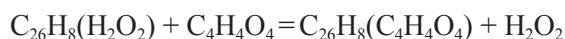
This reaction showed that under the influence of heat, fluorenic alcohol lost water and

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[11] A German chemist who studied under Hermann Limpricht and Friedrich Wöhler; well-known for the reaction that carries his name, used for the synthesis of alkylbenzenes.

became ether, being the first alcohol that behaved in this manner (Barbier, 1875).

As mentioned below, the discovery of fluorene and the synthesis of many of its derivatives were the subject of Barbier's doctoral thesis. The results were published as a long memoire (60 pages) divided into two sections, each divided into four chapters. The first part discussed the preparation of fluorene and its properties, its bromo and nitro derivatives, the products of oxidation, the composition and constitution of fluorene, and its possible synthesis. The second part discussed the mode of formation of hydrocarbons of formula $C_{28}H_{10}$ by the action of heat upon hydrocarbons of formula $C_{28}H_{14}$ derived from the double molecule of toluene with elimination of hydrogen (i.e. dibenzyl, stilbene, tolane, ditolyles, benzylxylene), and the work done on phenanthrene (Barbier, 1876).

3.2 Turpentine

According to Barbier, it was known that distillation of the products of the reaction between camphor and phosphorus pentachloride resulted in their decomposition; they lost HCl and yielded *p*-cymene (Barbier, 1872). The same phenomenon took place with certain derivatives of turpentine; they also produced *p*-cymene or one of it isomers. Barbier reacted terpine, $C_{20}H_{20}O_4 + H_2O_2$ (actually $C_{10}H_{20}O_2 + H_2O$) with bromine and obtained a slightly yellow semi fluid derivative, which seemed to be a brominated derivative of terpene. This compound was decomposed by distillation into a large amount of HBr and a hydrocarbon, which had all the characteristics of *p*-cymene. It was a colorless liquid, smelling strong like citron, boiling between 176° to 179 °C, and relative density 0.864 at 15 °C. Elemental analysis indicated that it contained, by weight, 89.54% carbon and 10.51% hydrogen, the same as *p*-cymene (Barbier, 1872).

In addition to the subjects described above, Barbier studied the action of heat on aromatic hydrocarbons (Barbier, 1874ab) and acetones (Barbier and Roux, 1886); the synthesis of safranines and their derivatives (Barbier and Vignon, 1887ab); the synthesis and properties of a variety of new compounds (i.e. Barbier, 1888, 1898b, 1899a; Barbier and Bouveault. 1894a, 1895a); dispersion in organic compounds, in aqueous solutions, etc. (Barbier and Roux, 1889, 1890); the preparation of nitroguaiacol and amidoguaiacol (Barbier, 1899bd); the use of the organometallic catalysts with the Barbier reaction (Barbier, 1899a; Barbier and Grignard, 1907); published his point of view regarding the conflict with Grignard about the use of magnesium (Barbier, 1910); etc.

APPENDIX

Philippe Antoine Francoise Barbier

Barbier was born on March 2, 1848, in Luzy (Nièvre), France, the son of Germain François Barbier, a teacher, and Elisabeth Gros. Between 1869 and 1876 he served as chief of the laboratory of organic chemistry of Marcellin Berthelot (1827-1907) at the Collège de France. In 1876 the Faculty of Sciences of Paris awarded Barbier his doctoral degree in physical sciences after successfully defending a thesis about fluorene and its derivatives, a work carried on at the Collège de France, under the direction of Berthelot (Barbier, 1876). The examiners were Paul Quentin Desains (1817-1885), Henry Sainte-Claire Deville (1818-1881), and Louis Joseph Troost (1825-1911). Shortly thereafter, the École Supérieure de Pharmacy awarded him a degree of pharmacist of first class, after defending a thesis about coumarin, its synthesis, constitution, and properties (Anonymous, 2019; Barbier, 1879).

Between 1876 and 1878 Barbier was *préparateur*[12]at the École de Pharmacy de Paris, afterwards, maître de conferences at the Faculté des Sciences de Lyon (1878-1879), professor of chemistry at the Faculté des Sciences of Besançon (1880-1884), and professor of chemistry at the Faculté des Science de Lyon (1889 until his retirement in 1919). Barbier's most famous student was Victor Grignard (1871-1935; 1912 Nobel Prize in Chemistry) (Anonymous, 2019).

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[12] An assistant responsible for preparing the experiments conducted during a class.

Barbier served in many public offices and was awarded several important awards. Between 1879 and 1884 he served in the Commision Départamental d'Hygiène of Houbs, as inspector of pharmacies, and as administrator of the École de Agriculture. During 14 years he administered the École Professional La Martinienne and during 23 years he was a member of the Commission Météorologique Départemental of Rhom. In 1871 he was elected member of the Société Chimique de France, In 1889 he was appointed Officer d'Instruction Publique and in 1908 Chevalier du Mérite Agricole (two appointments awarded to distinguished academics). In 1908 the Académie des Sciences awarded him the Jecker Prize for his work in organic chemistry, in 1905 he was appointed Chevalier of the Légion d'Honneur and in 1908 promoted to Officier (Anonymous, 2019). Barbier passed away on September 18, 1922.

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