



Léon Prunier

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Resumen

Léon Prunier (1846-1906), a French pharmacist and physician, who studied the synthesis of polypropylene hydrocarbons by the reaction of propylene bromide with nascent hydrogen prepared by different means, and the synthesis of ethylene acetylene; proving that the latter was identical with crotonylene. Together with R. David, they synthesized a variety of high melting point unsaturated hydrocarbons by the pyrolysis of American petroleum. His main contribution was the study of quercitol, its preparation by means of lead acetate, its physical and chemical properties, as well as its reaction with a wide range of chemicals. He proved that the thermal decomposition of quercitol at high temperatures led to the synthesis of aromatic compounds, among them, hydroquinone, quinhydrone, and benzene.

Palabras clave

Bromides; crotonaldehyde; ethyl acetylene; hydrocarbons; quercitol and derivatives; unsaturated hydrocarbons.

Abstract

Léon Prunier (1846-1906), farmacéutico y médico francés, que estudió la síntesis de hidrocarburos del polipropileno mediante la reacción de bromuro de propileno con hidrógeno nascente preparado por diferentes medios, y la síntesis de etileno-acetileno; demostrando que este último era idéntico al crotonileno. Junto con R. David sintetizaron una variedad de hidrocarburos no saturados, de alto punto de fusión, mediante la pirolisis del petróleo americano. Su principal aporte fue el estudio del quercitol, su preparación mediante acetato de plomo, sus propiedades físicas y químicas, así como su reacción con una amplia gama de productos químicos. Demostró que la descomposición térmica del quercitol a altas temperaturas, conducía a la síntesis de compuestos aromáticos, entre ellos, hidroquinona, quinhidrona y benceno.

Keywords

Bromuros, hidrocarburos; hidrocarburos no saturados; quercitol y derivados.

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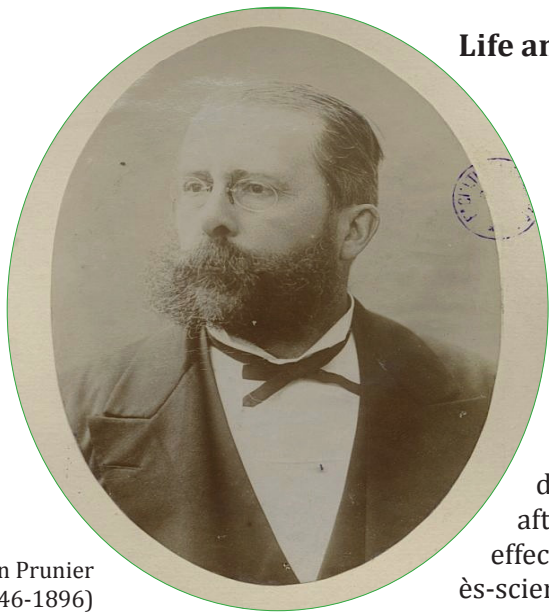


FIGURE 1. Léon Prunier (1846-1896)

Life and career

Very little information seems to be available about the early life of Léon Prunier (Figure 1). Prunier was born on August 26, 1841. After finishing his basic education, he entered the *École Supérieure de Pharmacie* in Paris from where he graduated as *pharmacien de 1^{ère} classe* after defending a dissertation about the unsaturated hydrocarbons generated during the industrial treatment of American petroleum (Prunier, 1879c). In the meantime, he earned the diploma of *licencié ès-sciences physiques*, the degree of *docteur ès-médecine* from the *Faculté de Médecine de Paris* after defending a thesis about the chemical and therapeutic effects of glycerin (Prunier, 1875c), and the degree of *docteur ès-sciences physiques* from the *Faculté des Sciences*, after defending a thesis about quercitol and its derivatives (Prunier, 1878b). Prunier tried three times, unsuccessfully, to earn the position of *agrégé* (the door to an academic career) at the *Faculté de Médecine de Paris*, after presenting theses about the physical theory of the production of heat in animals (Prunier, 1876a), the crystallin nitrogen principles in animal organisms (Prunier, 1878f), and the correspondence of chemical phenomena in vegetables and animals (Prunier, 1878g). The following year he succeeded in earning this position at the *École Supérieure de Pharmacie*, with a dissertation about the presence of opium alkalis in corpses (Prunier, 1879a). Prunier served as *agrégé préparateur* of the chemistry courses given by Alexandre-Edouard Baudrimont (1806-1880) at the *École Supérieure de Pharmacie* and eventually substituted him as professor of chemical pharmacy. He then took charge of the course of analytical chemistry, replacing Jacques Personne (1816-1880). Prunier also served as chief pharmacist of the *Hôpital du Midi et de la Maternité* (1869).

Prunier participated actively in scientific circles and public activities and was rewarded accordingly. He was member of the *Société de Pharmacie de Paris*, serving as its *Secrétaire* (1883), its *Vice President* (1885), and *President* (1886); member of the *Académie de Médecine*, section de pharmacie (1887), member and *President* of the *Société de Pharmaciens des Hôpitaux Civils*, and member of the *Council of the Société d'Encouragement pour l'Industrie Nationale*. He served as chief pharmacist and director of the *Pharmacie Centrale des Hôpitaux* (1897) until his death on August 12, 1906,

Scientific contribution

Prunier wrote about 30 papers and books (i.e., Prunier, 1878fg, 1879a, 1881, 1885ab; 1886-1889, 1889) about organic, inorganic, and electrochemistry, chemical synthesis, plant composition, mineral waters, etc. As customary to candidates to the *Académie de Médecine*, he published a booklet describing his research and results (Prunier, 1883).

Attention must be paid to the fact that Prunier used the old values for the atomic mass of the elements, for example, C = 6 (propene C_6H_6); H = 1, monoatomic; and HO = water.

Hydrocarbons

Prunier reported that treating propylene bromide, boiling from 138° to 143 °C, with nascent hydrogen provided by HCl and zinc, acetic acid and zinc, and the sodium amalgam, regenerated partially the propylene, but it also yielded several new polypropylene hydrocarbons. In every case, the reaction was clearly exothermic (Prunier, 1873a). He was able to remove from the residue a large amount of a viscous liquid, lighter than water and strongly smelling like impure methanol. This liquid, carefully dried, was attacked violently by bromine with almost total conversion into a very dense bromide, viscous, and partly crystallizable. Fractional distillation split it into a series of rather ill-defined portions, of which, the first was a liquid passing around 70°-80 °C. This liquid was mobile, colorless, and slightly odorous. At around 330°-340 °C, near 20% of the original liquid distilled as an almost colorless, slightly viscous body, and slightly lighter than water. Chemical analysis by combustion, indicated that it contained, by weight, 85.4% carbon and 14.0% hydrogen ($\pm 100\%$), that is, it was a hydrocarbon of the formula $C_{2n}H_{2n}$. In this case, it was a polymer of propylene $C_{6n}H_{6n}$, the various polymers of this formula arising simultaneously in the reduction of the bromide (Prunier, 1873a).

According to Prunier, the hydrocarbon boiling at around 70 °C, was probably dipropylene $(C_6H_6)_2$, its boiling point was like that of hexane (69 °C), while the hydrocarbon analyzed was hexapropylene $(C_6H_6)_6$. Both compounds belonged to the series of polypropylenes tetrapropylene $(C_6H_6)_4$ and pentapropylene $(C_6H_6)_5$, prepared by Marcelin Berthelot (1827-1907) when reacting propylene with concentrated sulfuric acid (Berthelot, 1869). Above 350 °C, Prunier also noticed the formation of polymers of even greater condensation than $(C_6H_6)_6$ (Prunier, 1873a).

The next project was related to the synthesis of ethyl acetylene and to prove that it was identical with crotonylene (Prunier, 1873b). Prunier wrote that Berthelot had prepared ethyl acetylene by reacting acetylene with ethylene at the temperature of dark red, according to $C_4H_2 + C_4H_4 = C_8H_6$ (Berthelot, 1866). This result led Prunier to test the possibility that ethyl acetylene was identical with someone of the hydrocarbons of the same formula, which had been obtained so far, with crotonylene, a hydrocarbon that Eugène Caventou (1824-1913) had prepared by removing from butylene dibromide, $C_8H_6Br_{2n}$, two equivalents of HBr (Caventou, 1863). This assumption was reinforced by Prunier's finding that large amounts of crotonylene appeared when heating red-hot petroleum hydrocarbons. In his first experiments, Prunier confirmed Berthelot finding that heating dark red a mixture of equal volumes of acetylene and ethylene resulted in the formation of ethyl acetylene. The resulting product reacted with bromine to yield its tetrabromide, $C_8H_6Br_4$. The purified substance appeared as needles or light patches, melting at 113°-115 °C, which distilled without decomposition. Chemical analysis (burning and titrating with silver bromide), indicated that it contained, by weight, 13.2% carbon, 1.9% hydrogen, and 85.3% bromine, a composition identical to the crotonylene described by Caventou. Prunier believed that it should also be possible to transform ethyl acetylene into crotonic aldehyde by the same process, which Berthelot had used to convert ethylene to ordinary aldehyde (Prunier, 1873b).

In 1878 Prunier and R. David visited the 1876 World Fair in Philadelphia and got familiar with Herbert Tweddle and his work on the distillation of petroleum and the separation of a variety of new paraffins having very high melting points. They were fortunate to obtain from Tweddle several kilograms of his petrocene, which by sublimation provided a yellowish green body known as thallene, and by fractional crystallization, other products (carbocene, carbopetrocene, etc.) distinguished by their high melting point. Prunier and David decided to make a more detailed study of these products and as those arising from the redistillation of natural oils (Prunier & David, 1878).

Their first results indicated that all the above products were mixtures and not pure substances, which could be resolved into saturated (paraffins) and unsaturated compounds by means of appropriate solvents. Treatment with bromine and sulfuric acid allowed determining the relative portion of unsaturated components (85 to 95%). Anyhow, all the starting materials were characterized by high relative densities, for example, petrocene, 1.206, and the paraffins, by their high melting point, 70^o to 85 °C. Chemical analysis indicated that the unsaturated fraction contained substances such as anthracene, phenanthrene, chrysene, chrysogene, etc., characterized for their high carbon content (88 to 96%) (Prunier & David, 1878).

In a following paper, Prunier mentioned that using solvents he was able to isolate a green, granular, and crystalline mass, soluble in carbon disulfide and hot chloroform, except for a slight carbonaceous residue, amounting to less than 3% of the mass. Evaporation of the solvent left a reddish-brown powdery containing, by weight, 97.09% carbon and 3.3% hydrogen, corresponding to the formula $(C_{12}H_2)_n$. These figures indicated the presence of an extremely high-order unsaturated compound. Further work indicated that this mass was a mixture of various crystallized hydrocarbons, extremely rich in carbon and constituting a completely new category, having composition similar to that of the coals themselves (carbon black, coke from gas retorts, etc.) (Prunier, 1879bc).

For example, using alcohol containing a little of chloroform, yielded a white hydrocarbon of a very brilliant pearly luster, precipitating from its solution in a silky and moiré state, and crystallizing in extremely fine needles, melting at around 260 °C, being very electric, and endowed with a very intense blue fluorescence. It was sparingly soluble in hot alcohol, ether, and chloroform, and soluble in petroleum, benzene, carbon disulfide, and boiling acetic acid (Prunier, 1879bc).

Chemical analysis by combustion indicated that it contained, by weight, 97.04% carbon and 3.07% hydrogen, corresponding to the formula $(C_{12}H_2)_n$. Prunier tried unsuccessfully to determine the value of n (Prunier, 1879bc).

According to Prunier and E. Varenne, the above results suggested the possibility that the coke forming the residue contained still higher hydrocarbons. To test this hypothesis, they used a material, which was strongly blistered, shiny black, very brittle, had relative density close to 2.0, and after incineration left very little cinder, composed mainly of calcium carbonate. This coke, treated with solvents, left an insoluble residue of carbon, properly so called, which retained a certain quantity of the solvent. Chemical analysis indicated that it contained from 97.4 to 98.0% carbon. The dry filtrate contained 97.7% carbon and 2.5% hydrogen. These figures suggested that its possible formula was $(C_{14}H_2)_n$ (Prunier & Varenne, 1880).

Prunier and Varenne fractionated by distillation the extract obtained with carbon disulfide and found that most of the compounds passing below 400 °C were soluble in alcohol, ether, or acetic acid. These products were all strongly fluorescent and contained oxygen. Distillation above 450 °C, left a residue formed of three quarters of the original mass, which was completely soluble in chloroform and carbon disulfide. (Prunier & Varenne, 1880).

All the above information led to Prunier's thesis to obtain the diploma of pharmacist of first class (Prunier, 1879c). The conclusions of the publications were repeated in an extended form in his thesis.

The first conclusion was that light paraffinic oils, of formula $C_{2n}H_{2n+2}$, subjected to pyrogenic dissociation, became an abundant source of unsaturated hydrocarbons belonging mainly to the two series $C_{2n}H_{2n}$ and $C_{2n}H_{2n-2}$, among them, ethylene, propylene, butylene, and acetylene. These compounds were less rich in carbon (percentagewise) than the saturated hydrocarbon, which gave them birth, but capable, under the action of prolonged heat, of recombining with each other to give rise to increasingly complex compounds. That is, they were accompanied almost simultaneously by subsequent products of their polymerization or their reciprocal combination, for example, benzene, ethyl acetylene, or crotonylene. The latter was usually obtained in a relatively considerable proportion (Prunier, 1879ab).

These assumptions were confirmed experimentally, particularly by the synthesis of crotonylene tetrabromide, $C_4H_2(C_4H_4)Br_4$, by ethylene and acetylene combined in equal volumes, the synthesis of butyl acetylene $C_4H_2(C_8H_8)$, and amyl acetylene $C_4H_2(C_{10}H_{10})$, etc. In these experiments, a stream of light hydrocarbons (boiling between 50° to 60 °C) was passed through a porcelain tube heated dark red and the outgoing gases flown through a series of refrigerated absorbing flasks where bromine retained the unsaturated compounds originated by the pyrolysis. The deprived vapor had an agreeable odor, quite different from that of petroleum; it was not condensed by a mixture of ice and salt and burned with a brilliant flame. The primitive stream generated mainly the bromides of propylene, butylene, and amylene, which were separated by fractional distillation into compounds belonging to the three series $C_{2n}H_{2n}Br_2$, $C_{2n}H_{2n-2}Br_2$, and $C_{2n}H_{2n-2}Br_4$. The byproduct of the distillation, $C_8H_6Br_4$, was particularly interesting. It was crystalline, melted at 114 °C, and constituted most of the residue of the distillation above 180 °C (Prunier, 1879ab).

Prunier tried and succeeded in regenerating propylene and butylene by means of nascent hydrogen prepared from the reaction of HCl with zinc, acetic acid and zinc, and the sodium amalgam. The reaction with acetic acid and zinc produced as byproduct, various propylene polymers, among them, di-, tri-, tetra-, and penta-propylene (Prunier, 1879ab).

Prunier found that selective solvent extraction was better than fractional distillation for separating the components boiling between 350° and 450 °C. He found that boiling alcohol dissolved only part of the components of the mixture, while the others dissolved completely in an excess of ether, carbon disulfide, chloroform, and benzene (the thesis gives a detailed description of the procedure). In this way, he was able to resolve each of the industrial products into many hydrocarbons, among them anthracene, phenanthrene, chrysene, pyrene, chrysogene, benzerythrene, fluoranthene, parachrysene, etc., all of them containing about 95% carbon. In addition to these compounds, Prunier also obtained a variety of new compounds containing 96 to 97% carbon, that is, approaching the actual coals, such as black smoke, retort charcoal, etc. This suggested the possible existence of

the following series: $(C_8H_2)_n$, $(C_{10}H_2)_n$, $(C_{12}H_2)_n$, and $(C_{14}H_2)_n$, containing 96.00%, 96.77%, 97.29%, and 97.67% carbon, respectively, the value of n being variable, but generally greater than 4 (Prunier,1879ab).

Quercitol

In 1849, Paul Laurent, professor at the Forest School of Macy, asked Henri Braconnot (1780-1855) to examine the acorns of the oak trees *Quercus racemosa* and *sessiliflora*. Braconnot agreed, thinking that at the same time he might find a procedure to clean the acorns collected in France of tannin, which made them acerbic, a goal he was unable to achieve (Braconnot, 1849). Braconnot crushed fresh acorns deprived of their outer envelope, in a marble mortar with successive small quantities of water until he obtained a homogenous porridge. The filtrated liquid, free of the suspended starch, was found to ferment and generate a low acidity. The liquid produced precipitates with acids, limewater, barite water, and alcohol. The precipitate formed by very diluted sulfuric was purple-yellow, tasteless, and becoming sour when stored in a stoppered flask. Ferric sulfate turned it black, due to tannin. Dried it burned with a lot of flame, due to a fatty substance, and left a charcoal, which resisted a long sustained red heat (Braconnot, 1849).

Braconnot was particularly interested in an intermediate precipitate of hard, sandy white crystals, mixed with a very divided earthy salt. The grainy crystals could be easily separated by boiling water. The latter could be isolated by washing with boiling water. Evaporation of the liquid resulted in the precipitation of crystals in semi-transparent parallelepipeds, unalterable to air, hard, crunchy to the bite, of a slightly sweet earthy flavor, and soluble in a large amount of cold water. Heated slightly, they melted without decomposing and left after cooling a solid, semi-transparent, and colorless mass. At a higher temperature, this matter turned yellow, gave off a caramel odor, and turned into an extractive substance, very soluble in water. Further heating led to carbonization and burning without leaving any residue. The same crystalline matter, dissolved in water mixed with a little yeast, did not go through alcoholic fermentation. All these resulted indicated that the material behaved like milk sugar (lactin), which was only slightly different from that of the milk of mammals, roughly, for example, as legumin differed from casein (Braconnot, 1849).

Braconnot treated his products with a variety of chemical reagents and calcination, and concluded that the peeled acorns contained, by weight, 31.80% water, 36.94% starch, 1.90% lignin, 15.82% animal matter (legumin) combined with tannin; 5.00% extractive matter; 7% non-crystallizable sugar, an undetermined amount of milk sugar (lactin), 3.27% of a fixed oil, an undetermined amount of citric acid; 0.38% KOH; 0.05% potassium sulfate; 0.27% calcium phosphate; 0.19% potassium sulfate; 0.01% potassium chloride; and traces of silica and iron oxide (Braconnot, 1849).

Braconnot speculated that his results were proof enough that the cotyledons of acorns contained all the elements of milk: they not only held milk sugar, but also a considerable quantity of caseous matter, a somewhat extractive nitrogenous matter, a high proportion of calcium phosphate, as well as the soluble salts present in milk, and finally, a fatty substance not having, in truth, the consistency of butter (Braconnot, 1849).

Two year later, Victor Dessaignes (1800-1885) carried additional experiments and proved that the sugar contained in acorn was not lactin but one intermediate between

mannitol and dulcitol (Dessaignes, 1851). Dessaignes took a few grams of the sugar, recrystallized it several times with diluted alcohol and obtained transparent prisms, which heated to 210 °C, it did not lose any weight. They melted at 225 °C and then emitted vapors, which condensed into a weak crystalline sublimate. At this high temperature, a small amount of the sugar changed and turned into a black substance; the remainder crystallized unchanged after dissolving in water. It reacted with ordinary warm nitric acid, yielding only oxalic acid. Rubbed together with concentrated sulfuric acid, it dissolved without coloring, and formed a paired sulfoconjugated acid, the calcium salt of which did not crystallize. With a mixture of concentrated sulfuric and nitric acid it formed a detonating nitro compound looking like a white resin, insoluble in water, soluble in hot alcohol, but non-crystallizable, and thus differed from nitromannitol. Heated with KOH it did not change its color and did not give off a caramel odor; boiled with a solution of copper acetate, it did not reduce the copper. It was not precipitated by basic acetic acid lead oxide, but addition resulted in a copious non-crystallizable precipitate. It did not ferment with brewer's yeast. Burnt with copper oxide potassium chlorate indicated that it contained, by weight, 43.60% carbon, 7.60% hydrogen, and 48.79% oxygen, corresponding to the formula $C_{12}H_{12}O_{10}$, that is, mannitol minus the elements of water. According to Dessaignes, his results proved clearly that the acorn sugar was a new special and well-characterized kind of sugar (Dessaignes, 1851). According to Prunier, Dessaignes asked and received the approval of Braconnot to name the new sugar *quercite* (quercitol) (Prunier, 1878e).

Prunier wrote that all the published information about quercitol described its properties and characteristics, but none had deciphered the chemical functions present in its constitution. This missing piece was completed by Berthelot, who discovered that quercitol was a dextrorotatory penta alcohol (Berthelot, 1855, 1856). According to him, experience indicated that many immediate principles were characterized by their aptitude to split into simpler compounds under the action of ferments and other reactants. The combination of the split products represented the composition of the primitive body, usually increased, or decreased by the elements of water. A typical example was the hydrolysis of fatty materials, yielding acids and glycerin with fixation of 1, 2, or 3 molecules of water. Berthelot extended this idea to the formation of neutral esters by sweet materials, under the influence of acids. According to Berthelot, sweet substances could be divided into two large categories, having different stability. The first included glycerin, mannitol, dulcitol, pinitol, quercitol, erythroglucin, etc., all stable compounds, generally more or less volatile, capable of withstanding the influence of a temperature of 200° to 250 °C, as well as the action of strong acids and alkalis at a temperature of 100 °C. All these substances enclosed an excess of hydrogen over the proportion necessary to form water with their oxygen. The second category contained sugars, which were fermentable directly or indirectly in contact with yeast (cane sugar, fructose, glucoses, lactic acid, lactose, melitose, etc.), and other isomeric bodies, which did not ferment (sorbitol, eucalyn, etc.). All these substances were decomposed by heating at 200 °C and by strong mineral acids and alkalis at 100 °C. They were all sweet, very soluble in water, contained hydrogen and oxygen in the proportions necessary to form water, formed with strong bases particular derivatives, and combined with acids in several proportions generating neutral substances (Berthelot, 1855, 1856).

Berthelot reported the reaction of several of these sweet materials (mannitol, dulcitol, pinitol, quercitol, erythritol, orcin, and cane sugar) with different acids (i.e., HCl, nitric, sulfuric, phosphoric, acetic, butyric, benzoic, stearic, etc.), as well as the properties

and formulas of the resulting esters. In the case of quercitol, he reported the formulas $C_{12}H_{12}O_{10} = 2C_6H_6O_5$; for quercitol; and $C_{12}H$ for quercitol stearate (Berthelot, 1855, 1856).

Berthelot added that heating quercitol to 200⁰-250 °C with stearic or benzoic acids, formed neutral esters comparable to fatty materials. The existence of a penta-acetic, -butyric, or -hydrochloride established that quercitol was a penta-alcohol (Berthelot, 1872).

Berthelot suggested to Prunier to continue his work on the subject, which Prunier did and as a result he published a series of papers (Prunier, 1875b, 1876b, 1877abc, 1878acd), which culminated in his doctoral thesis (Prunier, 1878b). The thesis included the preparation of quercitol, its physical properties, the action of heat and KOH, the preparation of the derivatives formed with HCl, acetic acid, butyric acid, hydrogen iodide, and hydrogen bromide.

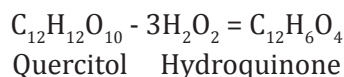
Prunier wrote that quercitol could be prepared by two methods: (a) Braconnot's procedure, and (b) by means of lead acetate. As mentioned before, in Braconnot's method the nude acorns were ground and then extracted with cold water, to separate the soluble components. Done with warm water resulted also in the solution of the starchy substances. This procedure required the use of substantial amounts of water (10 liters for each 1.5 kg of acorns) that had to be eliminated by evaporation under vacuum. The concentrated liquor was then fermented with beer's yeast to destroy the accompanying sugars, followed by boiling with limewater to precipitate the tannin, the nitrogenous components, and the small amount of starch dissolved, bleaching with animal charcoal, and purification by recrystallization. The Braconnot process was laborious and of low yield (about 1 to 1.5 thousandth of the original weight of acorns) (Prunier, 1878bd).

The second procedure was based on the property of basic lead acetate of precipitating most of the foreign material present in the acorn, among them, chlorides, sulfates, carbonates, and starchy matter, which otherwise would dissolve in cold water. Quercitol remained in the liquid. After the fermentation and bleaching stages, the remaining lead acetate was precipitated by means of a stream of CO₂ or diluted sulfuric acid. The quercitol was then purified by repeated crystallization from dilute alcohol. The many combinations of quercitol with the metals present in the solution were split with a diluted solution of HCl. Prunier remarked that one important source of loss was fermentation of the quercitol not by the beer's yeast but by a champignon belonging to the genre *Spicaria* (Prunier, 1878bd).

Prunier wrote that quercitol belonged to the fifth crystallographic system or clinorhombic, was dextrorotatory with $[\alpha]_D = 24^{\circ}17'$, a value that was not affected by dilution and by the temperature between 15° to 70 °C. The relative density of solid quercitol was 1.5845 at 13 °C. Prunier determined the relative density at 20 °C of a series of aqueous solutions containing from 2 g (d = 1.0136) to 12.400 g (d = 1.0540) of quercitol per 100 g of solution. Quercitol was partially soluble in water, was insoluble in alcohol (cold or boiling), ether, benzene, and chloroform, and completely soluble in diluted HCl (Prunier, 1877c, 1878bd).

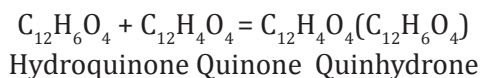
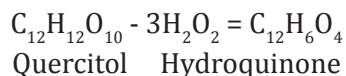
Put over a heated platinum plate, quercitol pure melted into a colorless liquid, which caught fire in contact with a flame, and burned with a brilliant flame similar to that of glycerin (Prunier, 1875a, 1878bd). Quercitol was a polyatomic alcohol, hence it was expected that upon heating it would lose water and provide several anhydrides and derivatives, in the same manner as mannitol and glycerin. This assumption was confirmed experimentally. Dehydrated at room temperature in the presence of sulfuric acid, showed

no changes, but done at temperatures increasing above 100 °C showed that the proportion of carbon increased progressively from the original value of 43.7 corresponding to the formula $C_{12}H_{12}O_{10}$, up to a maximum of 45.01%, while the hydrogen decreased from 7.5 to 7.3%. These results corresponded to the loss of H_2O_2 for 4 molecules of quercitol: $4C_{12}H_{12}O_{10} - H_2O_2 = C_{46}H_{46}O_{38}$. At about 230 °C, the quercitol melted while releasing a sublimated composed of crystals of different nature, which condensed on the walls of the flask. Prunier was unable to determine the composition of the many products formed. This problem was solved by conducting the process under a pressure of 2 cmHg. One of the products formed at 250 °C was found to contain, by weight, 46.44% carbon, 7.5% hydrogen, and 46.06% oxygen, corresponding to $C_{25}H_{12}O_{18}$. This substance melted at about 228°-230 °C, it was less soluble in water than quercitol, even less in alcohol, and totally insoluble in ether. According to Prunier, at a temperature of 280°-290 °C the thermal decomposition of quercitol started to generate aromatic compounds, for example (Prunier, 1875a, 1878bd):



Next, part of the hydroquinone lost hydrogen and generated quinone, $C_{12}H_4O_4$. The quinone combined with hydroquinone, forming quinhydrone $C_{12}H_4O_4(C_{12}H_6O_4)$. According to Prunier, the results indicated that the thermal decomposition of quercitol yielded two series of very different compound: (a) Between the melting point and 250 °C, the substances volatilized, as well as the residue, were insoluble in ether, soluble in water, and susceptible of regenerating quercitol by prolonged boiling, and (b) from 260° to 275 °C, the products were very soluble in ether and incapable of regenerating quercitol by boiling (Prunier, 1875a, 1878bd).

Prunier reported that quercitol did not react with aqueous solutions of caustic alkalis, even when boiling. The result was completely different at temperatures above 220 °C; now, a strong reaction took place, with release of a gaseous mixture of water vapor and hydroquinone and a piquant smell of quinone, represented by the equations (Prunier, 1878bcd):



Prunier reported that quercitol monoacetate was easily prepared by the reaction of glacial acetic acid and quercitol. The triacetin ester was prepared by heating a mixture of one part of quercitol with 8 to 10 parts of acetic acid and 1 to 2 drops of acetic anhydride. This ester was colorless, bitter, insoluble in water and soluble in ether and in alcohol. The penta-acetate was prepared by reacting for several hours, quercitol with a slight excess of acetic anhydride, at 150 °C. Quercitol penta-acetate was a colorless and amorphous solid, bitter, having an agreeable odor. It was little soluble in water, more in alcohol, and very soluble in ether. The preparation of the butyric ester was much easier and did not require the use of acetic anhydride. Quercitol monobutyrate was prepared by reacting in a sealed tube at 110°-115 °C a mixture of one part of quercitol and 2 to 3 parts of butyric acid. This ester was slightly bitter, soluble in ether, less soluble in alcohol, and lesser in water. It was also soluble in acidified water. The tributyrates were prepared by heating to 150°-160 °C a

mixture of one part of quercitol with 10 to 15 parts of butyric acid. This ester was non-crystallizable, syrupy, colorless, and bitter. It was soluble in ether and alcohol. The penta ester was prepared by heating the residues of the preparation of the mono and tri esters with an excess of butyric acid in the ratio 1: 20. The ester was a syrupy substance, bitter, very soluble in ether and alcohol, and little in water (Prunier, 1877b, 1878bd).

Prunier reported that HCl acted upon quercitol in three ways: (1) diluted, it dissolved in large amounts, without reaction, even up to 100 °C. Evaporation of the solution left the quercitol crystallized, which explained why this acid was a very good agent for purifying the sugar; (2) concentrated, it generated the first products of substitution of HCl by the elements of water; and (3) in the form of a saturated aqueous solution, the attack was deeper and more complete. Quercitol was dehydrated to quercitane, $C_{12}H_{10}O_5$, or more derived chlorine compounds. Prunier described the synthesis of quercitol and quercitane monohydrochlorides, quercitol tri- and penta-chlorides, their properties, and formulas (Prunier, 1878abd).

Additional information referred to the action of hydrogen bromide and hydrogen iodide upon quercitol, the pertinent derivatives, and their properties. These acids acted in a different manner: Hydrogen bromide acted as a dehydrant and reductor, leading to the formation of benzene, phenol, and a variety of brominated compounds. Quercitol transformed into benzene through the intermediate compound, hydroquinone. The reaction of quercitol with hydrogen iodide led to the formation of benzene pure (Prunier, 1875b, 1876b, 1878bd).

Miscellaneous

Isobutyl chlorides

Prunier reacted dry chlorine with cold isobutyl iodide and observed that the first effect was formation of isobutyl chloride and precipitation of iodine. Prolongation of the process resulted in the synthesis of iodine chloride and substitution of hydrogen atoms by chlorine. The reaction was exothermic; towards the end the temperature rose to 80 °C while the liquor discolored noticeably and iodine trichloride formed (Prunier, 1875a). The solid phase, containing the various chloro substituted bodies, was filtered, dried, and distilled under vacuum (4 to 5 cmHg) and 140 °C, without decomposition. This process indicated several fixed points, one at 72 °C (corresponded roughly to 145 °C, under normal pressure), another around at 95 °C, a third around 112°-115 °C, a fourth around 130 °C, and a fifth one from 146° to 148 °C. Decomposition began at temperatures between 200° and 240 °C, with production of abundant fumes and formation of a charred residue, which solidified on cooling. Analysis of the body passing at 146°-148 °C (in vacuum) indicated that it contained, by weight, 17.0% of carbon, 1.5% of hydrogen, and 82.28% of chlorine (100.78%), corresponding approximately to the formula $C_8H_4Cl_3$. Prunier reported that the relative density at 18 °C of the pertinent products, increased as the boiling point increased, from 1.16 for the body boiling at 72 °C to 1.8 at 160 °C (Prunier, 1875a).

Butyl glycerin

In the following work, Prunier studied the possibility that that his compound, $C_8H_7Cl_2$, worked as an alcohol trichlorohydrin triatomic. For this purpose, he heated in a sealed tube a mixture of one part of the dichloride with 20 parts of water and noted that a significant amount of the chlorinated product dissolved, accompanied by the formation of a large amount of HCl (Prunier, 1884). After cooling, the acid was mostly neutralized with silver chloride and the liquid evaporated under vacuum. The remaining liquor was slightly colored, slightly acid, and deliquescent. The remaining acidity was eliminated with calcium carbonate and then extracted repeatedly with absolute alcohol and again evaporated under vacuum. The residue was yellowish, deliquescent, did not react with tournesol, and eventually solidified. In the end it solidified neutral to tournesol. Chemical analysis by combustion indicated that its composition corresponded to the formula $C_8H_{10}O_6$ (Prunier, 1884).

These results led Prunier to investigate the possibility of synthesizing the saturated ester of a triacid. For this purpose, he heated his new compound with acetic anhydride at a temperature of 140 °C; the ether produced was then isolated by the conventional method of Berthelot. The resulting compound, slightly yellow, neutral, and bitter, was saponified with titrated barite water and analyzed. The results indicated that it contained 75.09% of acetic acid combined, and a composition that corresponded almost to the formula $C_8H_4(C_4H_4O_4)_3$, that is, butyl triacetin containing 77% acetic acid. Prunier assumed that the excess of acetic acid was due to the presence of a large amount of a triacetin ester (Prunier, 1884).

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