



## Louis Armand Victor Amedée Cailliot

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### Abstract

Amédée Cailliot (1805-1884), a French physician and pharmacist who isolated for the first time several new acids (among them terephthalic) from turpentine, prepared a series of double salts of mercuric cyanide and potassium (and sodium) bromide and several derivatives of pimaric acid.

### Keywords

abietin, alkaloids, mercury compounds, opium, pimaric acid, terephthalic acid.

### *Louis Armand Victor Amedée Cailliot*

### Resumen

Amédée Cailliot (1805-1884), médico y farmacéutico francés que separó por primera vez varios ácidos nuevos de la trementina (entre ellos el ácido tereftálico), preparó una serie de sales dobles de cianuro mercuríco con bromuro de potasio (y sodio) y alcaloides y varios derivados del ácido pimárico.

### Palabras clave

abietín, alcaloides, compuestos de mercurio, opio, ácido pimárico, ácido tereftálico

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## Life and career

Amedée Cailliot was born on April 30, 1805, in Brest, Finistère, the son of Louis Calliot, the chief physician of the French Navy. After finishing his basic studies he entered the Faculty of Médecine of Strasbourg where he served as chemical assistant after presenting an essay about the resins from the Strasbourg fir (Cailliot, 1828a). He obtained his doctorate in 1830 after successfully defending a thesis about turpentine from firs of reverse cone (Cailliot, 1830). Shortly thereafter he was appointed head of chemical, physical and pharmaceutical works at the Faculty and in 1834 he won by competition a position of *agrégateur* at the same place after presenting a dissertation about the influence of atmospheric air upon the phenomena of life (Cailliot, 1834). In 1838 he was promoted to the chair of medical chemistry [Replacing Marie-Gabriel Masuyer (1761-1849)], after successfully defending a thesis about the history and appreciation of the progress of chemistry during the nineteenth century (Cailliot, 1838). He kept this position until 1871. During his tenure he established the first French laboratory of practical work in chemical medicine. In 1872, after the annexation of Alsace to Germany, he retired to Paris to work in the laboratory of Charles-Adolph Würtz (1817-1884), one of his former students. In 1830 he married Josephine Eléonore Meunier; two children were born of this union: Edouard and Claire Elisabeth. Cailliot passed away on November 21, 1884, in Paris.

Cailliot served as municipal councilor of Strasbourg and as honorary professor of the Faculty of Medicine of Nancy. In 1856 he was appointed chevalier of the Légion d'Honneur.

## Scientific contribution

Cailliot wrote about 15 papers on the subjects of inorganic, analytical, and organic chemistry, and natural products. In addition to the subjects described below, he carried on numerous legal tasks on toxicology, for example, on the advantages and dangers of using chloroform as an anesthetic (Tourdes et al., 1852).

In all that follows it is necessary to take into account that Cailliot wrote his chemical formulas and reactions using as atomic masses the values C = 6; O = 8; H = 1; and Cl = 35.5.

### *Potassium iodide*

Cailliot wrote that nowadays potassium iodide was a product widely used in medicine and the usual procedures for its preparation were time consuming and required careful manipulation to avoid the formation of byproducts. The traditional synthesis procedures involved reacting iodine with potassium hydroxide or the previous transformation of the iodine in hydrogen iodide. The first method was always accompanied by the simultaneous formation of potassium iodate, a byproduct easily separated because of its low solubility, or by heating to convert it into iodide. Unfortunately heat transformed part of the iodate into iodine. The second procedure involved the conversion of the iodide into HI by means of phosphorus or hydrogen sulfide, followed by neutralization of the acid with KOH. This method was very efficient but also very expensive (Cailliot, 1822, 1823).

Cailliot developed an alternative method based on the reaction of iodine with iron and decomposition of the resulting ferric iodide by means of potassium carbonate, as follows: Four parts of iodine were mixed with 2 parts of iron filings and 20 of water until the

solution, initially having a strong brown color, became colorless. The liquor was then put in a glass or porcelain vessel and heated to boiling. At this point was added a solution of pure potassium bicarbonate until no precipitate was formed, or a slight excess of potassium carbonate saturated with HI. The resulting solution was filtered and the precipitate washed with water until the wash showed no reaction with mercuric chloride. The filtrate was combined with all washes and slowly evaporated to dryness (Cailliot, 1822, 1823).

The same procedure could be used to prepare the iodides of sodium, magnesium, calcium, barium and strontium. The iodides of mercury could be prepared by reacting mercurous nitrate (or mercuric chloride) with the solution of ferric iodide (Cailliot, 1822, 1823).

### *Mercury compounds*

When trying to detect the presence of mercuric cyanide by means potassium iodide, Cailliot was very surprised to note the formation in the liquid of a large number of white pearly crystals, instead the expected precipitate of mercuric iodide (Cailliot, 1821). He separated the crystals, dissolved them in water, recrystallized the solution and obtained large plates, thin and brilliant, unaffected by the air, odorless in the dry state and smelling like bitter almonds when in solution, soluble in sixteen times their weight of water at room temperature, and more in hot water. They were also soluble in about ninety-six parts of alcohol at 34% (0.847). The new compound could be heated to a temperature incapable of destroying it without losing weight and luster, indicating that it probably was anhydrous. At a sufficiently higher temperature it decomposed partially into cyanogen, mercury, and a greenish yellow vapor, mixed with mercurious iodide. The remaining potassium iodide was blackened by a little of finely divided charcoal. The new compound, in contact with strong and weak acids, such as benzoic, camphoric and arsenious acid, converted into mercuric iodide, with disengagement of HCN. Interesting enough, it was not attacked by HCN and CO<sub>2</sub>. In the presence of hydrogen sulfide it precipitated black mercury sulfide (*b*-HgS) with release of HCN. The aqueous solution of the new compound reacted with metallic bisulfates producing black precipitates, for example, addition of 24 parts of sodium bisulfite produced 13 parts of mercuric sulfide. Lead salts produced a yellow precipitate of lead iodide; the salts of mercuric dioxide a red precipitate of mercuric iodide, and chlorine and mercuric chloride a red precipitate soluble in an excess of the solution. Iodine dissolved in it, in so much the greater quantity as its solution was the more concentrated. KOH, NaOH, or ammonia, free or combined with an acid, did not decompose the compound. Initially Cailliot believed that his new compound was formed of one part of mercury cyanide and one of potassium iodide; but this assumption was rejected after finding that the addition of a slight excess of sulfuric acid resulted in the formation of an abundant precipitate of mercuric oxide and a supernatant fluid containing a small amount of mercuric cyanide (Cailliot, 1821).

In a following publication Cailliot and Corriol described a new chemical combination they had found between mercuric iodide and ammonia (Cailliot & Corriol, 1823). It was well known that chlorides and iodides presented very similar chemical properties; when one of them was affected in a certain manner by a given reagent the other reacted more or less in the same manner. For this reason they thought that it was reasonable to assume the existence of a compound of mercury, iodine, hydrogen, and nitrogen, similar to the one formed by the reaction between ammonia and mercuric chloride. This assumption was promptly verified by mixing an aqueous solution of potassium iodide of known

composition, with a large excess of an aqueous solution of concentrated ammonia: the solution of the iodide assumed instantly a whitish color and then separated into a liquid phase containing the KI dissolved in ammonia, and a red brown precipitate. The liquid was separated by decantation and left in contact with air. The spontaneous evaporation of the ammonia led to the precipitation of a multitude of white small needles. Cailliot and Corriol wanted to study this solid by separating it from the liquid and drying over paper or by slight heat; to their surprise that as soon as the solid had been detached from the liquid it decomposed completely into ammonia that dissipated into the atmosphere, and red colored mercuric iodide. This surprising outcome indicated that the compound was completely unstable in air and probably reacted rapidly and intensively with water and dilute acids. The results confirmed this supposition; the compound was completely destroyed by these reagents (Cailliot & Corriol, 1823).

Cailliot and Corriol tried unsuccessfully to determine the proportion of ammonia and mercuric iodide in their new compound. Finally they looked for means to prepare the compound as separate large crystals. For this purpose they introduced into a small glass flask a mixture of one gram of mercuric iodide and 90 grams of aqueous ammonia freshly distilled. After sealing, the liquor was left to react under agitation until the reaction was finished. The liquid was then separated and abandoned for five days in contact with the atmosphere. This extended period of time was enough to deposit a large number of long disentangled needles. One portion of the remaining liquid was mixed with an excess of acetic acid and then with hydrogen sulfide, which resulted in the precipitation of mercuric sulfide. Another portion was evaporated at soft heat until it became odorless. Treatment of the concentrated liquid with mercurous nitrate produced a yellow precipitate, while addition of a small amount of calcium carbonate led to the release of strong ammonia odor. These results showed the presence of the iodides of mercury and ammonia (Cailliot & Corriol, 1823).

In another publication Cailliot reported his results about the synthesis of double salts composed of alkaloid chlorides and mercuric chloride, chlorides with mercuric iodide, and dichlorides with mercuric cyanide (Cailliot, 1829). He found that adding a diluted solution of mercuric chloride to a solution of any chloride resulted in the formation of an abundant white clotted precipitate. This precipitate was slightly soluble in water and alcohol, was not crystallizable, remained unchanged in contact with air, and tasted like mercuric chloride and the chloride employed. Heating the precipitate originating from the chlorides of the alkalis of quinquina to a temperature slightly above 100 °C turned it into a yellow mass; higher temperatures decomposed it into ammonia salts, other substances, and a voluminous carbon residue. Cailliot analyzed in particular the precipitate formed by the reaction between cinchonine hydrochloride and mercuric chloride. Analysis of the anhydrous product showed it contained, by weight, 39.57% of mercuric dichloride (Cailliot, 1829).

Cailliot added that during his preliminary experiments he had noticed that morphine, brucine, narcotine, cantharidin, and other alkaloids were able to combine with mercuric chloride and form triple salts. These results suggested that substances like narcotine and cantharidin were able to take up HCl and saturate it. He illustrated this assertion with the following example: addition of a diluted solution of mercuric chloride to a solution of narcotine in HCl led to the formation of a white pulverulent precipitate while the acid original liquor became completely neutral. This result indicated that under certain circumstances narcotine assumed an alkaline character, became polarized against certain acids, and saturated them (Cailliot, 1829).

The iodides presented a similar behavior: The double salt was white and under moderate heat it became yellow like sulfur, particularly when the alkaloid was cinchonine or strychnine. In general, all the double salts prepared by the precipitation of organic iodides with mercuric iodide were non-crystallizable, almost insoluble in water and alcohol, and somewhat palatable. Heated in a progressive manner they fused disengaging violet vapors of iodine and decomposing into a variety of products. Cailliot reported that the iodo-hydrargirate of cinchonine iodide contained 42.67% per weight of mercuric iodide. He also found that of all the salts of alkalis, only the iodides and bromides were able of combining with mercuric cyanide. The cyano-hydrargirates were white light substances, non-crystallizable, unchanged in air, little soluble in water and alcohol, and convertible by acids into red mercuric iodide and HCN (Cailliot, 1829).

Cailliot summarized these findings as follows: (a) the organic salifiable bases, free or combined with HCl, reacted with mercuric chloride in the same manner as with ammonia or ammonium chloride; (b) narcotine was able to assume an alkaline character and combine with hydrogen chloride or iodide, under the influence of mercuric chloride or iodide; and (c) the organic iodides combined with the metallic iodides and with mercuric chloride or cyanide (Cailliot, 1829).

Cailliot found that the reaction of potassium chromate with mercuric bromide was highly incomplete, contrary to the one taking place between the chromate and all other soluble mercuric salts. This fact suggested the possibility of using the chromate to recognize the presence of chlorides in bromides (Cailliot, 1830). As an example, he mixed a certain amount of potassium bromide with one-sixth of sodium chloride, dried the mixture and added to it equal parts of mercuric sulfate and manganese dioxide. The resulting mass was finely ground and heated until decomposition. This process converted the bromide into mercuric bromide. The resulting mixture was dissolved in water and tested with a few drops of potassium chromate. If any chloride is present, a number of small red points of mercuric chlorate were immediately deposited (Cailliot, 1830).

In 1828 Cailliot communicated to the Société de Pharmacie de Paris that he had found that the mixing of mercuric cyanide with alkaline bromides led to the formation of double salts where the cyanide played the role of electro-negative element, the same behavior that took place with alkaline chlorides (Cailliot, 1828). Afterwards he gave a full description of the pertinent experiments (Cailliot, 1831): He mixed a solution of mercuric cyanide with another of potassium bromide and noted the immediate formation of a multitude of small white flakes, easily separated by decantation. These crystals were impregnated with a solution of one of the salts used in their preparation. Slight heating and dissolution in distilled water purified the crystals. Upon cooling the purified material crystallized as large thin flakes, having a brilliant silk appearance. Cailliot named the new material *potassium bromide cyano-hydrargyrate* (potassium mercury bromo-cyanide). This double salt was soluble in water and alcohol, and found to contain, by weight, 8.74% water. Treatment of its aqueous solution with salts of organic alkalis resulted in the formation of a mixture of the bromide of the alkali and mercuric cyanide. Potassium bisulfate and mercurous salts decomposed the salt into the sulfide and bromide of the metal while diluted nitric acid decomposed it into potassium nitrate, mercuric bromide, and HCN. The latter reaction did not decompose completely the mercuric cyanide, proving that the two components of the cyano-hydrargyrate were not combined in a simple stoichiometry ratio (Cailliot, 1831).

When heated in a closed porcelain crucible, the double salt decomposed into a mixture of gases, containing cyanogen, and a solid residue of carbon, potassium bromide, and potassium

cyanide. Additional experiments proved that the double salt contained one mole (Cailliot writes atom instead of mole) of mercuric cyanide (68.49% anhydrous weight), one mole of potassium bromide (31.51% anhydrous weight), and four moles of water (Cailliot, 1831).

Cailliot prepared very pure cyano-hydrargyrate of sodium bromide by dissolving in water equal proportions of mercuric cyanide and sodium bromide. This salt crystallized as large laminar needles having a brilliant silver-white color. It was not affected by humid air; in the presence of dry air it became less brilliant and lost its crystallization water. It was very soluble in water and alcohol and decomposable by acids and organic alkalis. Its analysis indicated that it contained one mole of mercuric cyanide, one of sodium bromide, and three of water. Cailliot used a similar procedure to prepare the cyano-hydrargyrates of strontium bromide and of barium bromide (Cailliot, 1831).

Cailliot summarized his results as follows: (1) alkaline bromides and the bromides of ammonium, quinine, and cinchonine formed with mercuric cyanide double salts of defined proportions; (2) cinchonine bromide was formed by one mole of HBr and one mole of cinchonine, and (3) the salts of organic alkalis could be used, together mercuric cyanide, to identify the presence of a small amount of an alkaline bromide mixed with a chloride of the same species (Cailliot, 1831).

Cailliot also studied in detail the reaction of an organic alkaline base (opium) with mercuric chloride (Cailliot, 1833). He wrote that not long before (his time), it was generally believed that when a vegetable product reacted in any way with a metallic salt, all other vegetable products reacted in the same manner. For example, it was known that an aqueous extract of opium reacted immediately with a solution of mercuric chloride and that the reaction of mercuric salts with extracts of other indigenous plants deprived the salts of part of their oxygen. Hence it was expected that the reaction of an aqueous extract of opium with mercuric chloride would also result in a reduction of the salt. Most physicians were skeptical of this explanation because they knew that mercuric chloride did not sensibly lose its medical properties, whether it was administered in combination with an aqueous extract of opium or in the state of a simple solution in distilled water (Cailliot, 1833).

This practical observation led Cailliot to verify experimentally the state of mercuric chloride after it had reacted with an aqueous extract of opium. For this purpose he mixed an aqueous solution of 16 grams of extract with another containing 0.4 grams of the salt; his calculations indicated that these quantities were such that if the extract were of a non-alkaline nature, the salt would transform completely into mercurious chloride. A brown, flocculent precipitate was instantly formed, which was left undisturbed for fifteen days to allow the vegetable substance to exert its full action on the metallic body. After this period of time Cailliot separated the precipitate and washed it repeatedly with water and alcohol to eliminate all soluble matters. The clean precipitate changed its color to black in contact with ammonia and to greenish yellow with diluted HI. The washings had a bitter, styptic taste, which resembled those of the salts of mercury and the alkalis of opium; treated with a very small quantity of potassium iodide (say, 0.05 grams per 32 grams of fluid) they produced a large amount of a white precipitate, slightly soluble in water or alcohol.

The supernatant fluid had a deep brown color and a metallic taste, which excited the salivary glands; left undisturbed for six weeks, it gave no traces of mercurious chloride. Treated with a fresh amount of mercuric chloride it produced a brown precipitate. Potassium iodide occasioned a precipitate, which turned reddish on the addition of sulfuric or hydrochloric acid.

According to Cailliot, these facts proved that during the reaction of mercuric chloride with an aqueous extract of opium a portion of this salt converted into mercurious chloride and another part united with the active principles of the opium forming more or less complex compounds (Cailliot, 1833).

### *Turpentine*

As mentioned before, Cailliot conducted two studies on the subject, the first one about the characteristics of the resin and turpentine derived from firs growing in the Strasbourg region, served as the subject of his candidacy for a position at the Faculty of Médecine (Cailliot, 1828), and the second, a general study of the turpentine derived from firs having reverse cones (true fir), the subject of his doctoral thesis (Cailliot, 1830). The fir varieties studied in both works were *Abies pectinata*, yielding the turpentine of Strasbourg, *Abies balsamea*, producing the turpentine of Canada, and *Abies excelsa*, the natural pitch of the Vosges.

After some general considerations about the characteristics of these resins, Cailliot suggested dividing them into two classes: (1) Acid resins, where the acidity is shown by their action upon litmus paper, alkaline carbonates, etc.; and (2) neutral resins, showing no action on litmus, being insoluble in alkalis, etc. Some of these resins were soluble in cold alcohol, others, named *sub-resins*, insoluble in alcohol.

In the first step, Cailliot steam distilled the turpentine of Strasbourg in order to separate as much as possible the essential oil (Cailliot, 1830). The remaining residue was the *cooked turpentine* and the remaining water. The water that passed over had a strong bitter taste and colored strongly the litmus tincture and contained a reddish extractive substance, soluble in water and alcohol, and a free acid, apparently succinic acid. In practice it was neutralized by ammonia yielding a crystalline salt, a yellow white precipitate with salts of barium and calcium, a yellow red one with ferric oxide, none with manganese salts, and a precipitate of ammonium succinate with ammonia. Paolo Sangiorgio (1748-1816) (Sangiorgio, 1804) and Louis René Lecanu (1800-1871) and Louis Serbat (Lecanu & Serbat, 1822) had already reported the presence of succinic acid in the products of the distillation of turpentine by direct fire, but they had assumed that it was a result of the heating process. Cailliot's experiment showed that it was already present in turpentine as such (Cailliot, 1830).

The *cooked turpentine* was extracted with cold absolute alcohol to dissolve the soluble resin; the remaining residue was the neutral resin. The alcohol extract was evaporated to dryness and the residue treated with twice its weight of potassium carbonate dissolved in water. Additional treatment of the solution led to the precipitation of a crystalline substance, which Cailliot named *abietin*. The same substance was separated from the three varieties of fir studied. Abietin crystallized as needles having a rectangular base; it was odorless, almost insipid, with a weak resinous taste. Abietin did no color the litmus tincture and the violet syrup and melted easily under the action of the sunrays. The resulting liquid was transparent, colorless and looked melted tallow; on cooling it solidified into a white, opaque, and crystalline mass. Abietin was insoluble in cold water; it melted in boiling water without dissolution. It dissolved readily in alcohol of 34° (relative density 0.847) and in every proportion in boiling alcohol, ether, petroleum ether, and concentrated acetic acid, and crystallized when the solvents were volatilized. It was insoluble in KOH (Cailliot, 1830).

The resin saponified by the potassium carbonate was precipitated by means of a warm solution of ammonia; Cailliot named it *abietic acid*. This acid resin was slightly bitter; it reddened litmus, was soluble in all proportions in alcohol, ether, and petroleum ether, and neutralized by alkalis. Heated to 55 °C it agglomerated into transparent globules, every similar to rosin. It combined with bases losing about 5% of its weight as water. Cailliot reported the preparation and properties of a series of abietates (potassium, sodium, ammonium, barium, strontium, calcium, magnesium, quinine, and morphine). The abietates of sodium, potassium, and ammonia, were non-crystallizable; the latter was easily decomposed by heat. Quinine abietate was prepared by adding a neutral solution of ammonium abietate to another of neutral quinine sulfate. This salt was white, flocculent, insoluble in water, very fusible, easily soluble in alcohol and ether but not crystallizable from their solutions. Morphine abietate was prepared in the same manner; it was a white flocculent solid, soluble in alcohol and ether; these solutions were very bitter and non-crystallizable (Cailliot, 1830).

According to Cailliot the essence of the turpentine of *Abies pectinata* and *Abies excelsa* had an agreeable aromatic odor and hot taste; they were non-crystallizable, even at -20 °C, and did not combine with alkalis. The neutral *insoluble* resins were little different one from another; they were white, pulverulent, without a distinct crystalline form, dry to the touch, tasteless and not acting upon litmus. They were insoluble in cold alcohol of 40°, in petroleum ether, and in alkaline solutions. The neutral *soluble* resin (abietin) crystallized as needles having a rectangular base; the faces were inclined along the axis, forming more or less an elongated pyramid. Abietin was odorless almost insipid, insoluble in water and very soluble in ether, naphtha, and acetic acid; it was very soluble in alcohol of 34°; its alcoholic solution has a slight bitter taste and did not act upon litmus and the violet syrup. Upon melted it produced a white transparent liquid, which on cooling became white, opaque and crystalline solid (Cailliot, 1830).

The volatile oils (essence) of *Abies pectinata* (Strasbourg) and *Abies excelsa* had the following composition by weight percent (Table 1):

	Turpentine from <i>Abies</i> <i>pectinata</i>	Turpentine from <i>Abies</i> <i>excelsa</i>
Volatile oil	33.50%	32.00%
Acid resin	46.3g	45.37
Abietin	10.85	11.47
Sub-resin (insoluble in alcohol)	6.20	7.42
Extractive matter and succinic acid	0.85	1.22
Loss attributed mainly to the volatile oil	2.21	2.52

**Table 1:** Composition of the essences of *Abies pectinata* and *excelsa*.

Cailliot wrote that the sample of the turpentine of *Abies excelsa* that he had examined was shady, slightly colored, had a bitter taste, and was less fluid than the one from Strasbourg. It was very probably mixed with *Abies pectinata*. He also gave a detailed description of the turpentine of *Abies pectinata*, *Abies excelsa*, *Abies balsamea*, *Larix europea*, and *Pinus maritima* and *sylvestris*.

According to Cailliot, scientists were undecided regarding the question if vegetable resins were formed as such in vegetables or were the result of an oxidation process of the essential oils. If this was so, could it possible to reproduce it in the laboratory (Cailliot, 1846a, 1847)? In order to answer this question Cailliot subjected the essence of turpentine

to three different oxidation processes: (1) the slow action of air, (2) the action of air under the influence of bases, and (3) the more rapid action of nitric acid (Cailliot, 1846a, 1847).

According to Cailliot, the reaction of nitric acid with the essence of turpentine was vigorous and followed a complex route, but treating a small amount of turpentine with a layer excess of acid diluted in water resulted in a calm reaction, easy to follow in a distillation apparatus. The products of the reaction were numerous; abundant sparkling nitrous vapors, together with  $\text{CO}_2$ , a substantial quantity of HCN, and a certain amount of almost unaltered oil of turpentine. The latter had not changed its properties, particularly its rotation power. Conrad Bromeis (1820-1862) and S. M. Roubourdin had examined the mother liquor remaining in the distillation retort (Berzelius, 1843; Roubourdin, 1844); Bromeis found it contained a new acid, which he named *turpentinic acid*, and Roubourdin, oxalic acid and in several cases quadroxalate of ammonia (Cailliot, 1846, 1847).

Cailliot stopped the controlled reaction after no more nitrous vapors were formed and found that the residue contained two products, a mother liquor and a resinous substance. The mother liquor was found to contain oxalic acid, HCN, which under the operating conditions seemed to occupy the place of ammonium oxalate, and three new acids. One of these acids had the formula  $\text{C}_{16}\text{H}_6\text{O}_8 = \text{C}_{16}\text{H}_4\text{O}_8 + 2\text{HO}$ , that is, it was an isomer of the phthalic acid discovered by Auguste Laurent (1807-1853) (Laurent, 1836) in the reaction between naphthalene and nitric acid. For this reason Cailliot suggested naming it *terephthalic acid* (Je proposerai de le nommer acide téréphtalique). Terephthalic acid was sufficiently distinct from phthalic acid, it was white, tasteless, and insoluble in water, alcohol and ether; when heated a portion sublimed without losing its hydrate water, while another portion decomposed into  $\text{CO}_2$  and benzene,  $\text{C}_{12}\text{H}_6$ . The acid was entirely converted into benzene and  $\text{CO}_2$  when heated with calcium hydroxide. Nearly all the salts of terephthalic acid crystallized and burned readily, diffusing the odor of benzene (Cailliot, 1846a, 1847).

The second acid separated from the mother liquor had an elemental composition corresponding to the formula  $\text{C}_{14}\text{H}_7\text{O}_4 = \text{C}_{14}\text{H}_6\text{O}_3 + \text{HO}$ , which Cailliot named *terebenzic acid*. It differed from benzoic acid by one additional equivalent of hydrogen, and in other respects resembled it very closely: It volatilized previously to melting, was sparingly soluble in cold water, dissolved more readily in boiling water, and separated on cooling in acicular crystals. It was very soluble in alcohol and ether. The salts of the new acid exhibited the same solubility as the corresponding benzoates. Notwithstanding these analogies, it was impossible to confuse the two; terebenzic acid decomposed in boiling water and formed on crystallization a disordered mass of needles, and not laminae like benzoic acid. The terebenzic acid melted at  $169\text{ }^\circ\text{C}$  and benzoic acid at  $120\text{ }^\circ\text{C}$ ; terebenzic ether possessed a very distinct odor of aniseed; it boiled at  $130\text{ }^\circ\text{C}$ , substantially lower than benzoic ether ( $209\text{ }^\circ\text{C}$ ) (Cailliot, 1846a, 1847).

The third acid contained in the mother liquor, *terechrysenic acid* ( $\text{C}_6\text{H}_4\text{O}_5 = \text{C}_6\text{H}_3\text{O}_4 + \text{HO}$ ), was very different from the two preceding ones; it formed an orange-yellow amorphous mass, was very deliquescent, and dissolved in every proportion in water, alcohol, and ether; its initial taste was strongly acid and subsequently astringent and bitter. It expelled acetic acid from its combinations and formed with a large number of bases salts soluble in water. It was nonvolatile; it decomposed on distillation, first into  $\text{CO}_2$  and a slightly colored liquid acid, subsequently into combustible gases and an oily yellowish substance, leaving a residue of compact coal. Its ether acid was a dark orange-colored viscous liquid, which released on distillation an ethereal, nearly colorless liquid, an oily

liquid and a residue of carbon. The terechrysantes had a yellow or orange red color and most of them were soluble in water (Cailliot, 1846a, 1847).

Cailliot examined in detail the resinous mass, which separated from the mother liquor, and found it to contain considerable quantities of terephthalic and terebenzic acids, and three substances, which in their physical and chemical properties were reminded those of the natural resins. The first,  $A = C_{40}H_{24}O_{20}$ , was insoluble in alcohol and alkalis and corresponded to the sub-resins; the second,  $B = C_{40}H_{20}O_{10}$ , was soluble in alcohol, insoluble in alkalis, and corresponded to the neutral resins, (e.g. abietin); the third acid,  $C = C_{40}H_{24}O_{16}$ , dissolved in alcohol and in alkalis and was very similar to rosin. In spite of these characteristics, they had a very different composition, as they contained more oxygen and less hydrogen. Cailliot believed that these three resins were very similar to those produced by the action of nitric acid upon natural resins. For example, treating pimaric acid with nitric acid yielded a substance insoluble in ammonia, soluble in alcohol, and appearing to be identical with the body B. The formulas of these resins suggested their ordering in two series, one comprising those containing resins having less than 20 equivalents of carbon, and another, including those resinous bodies, which contained 40 and more equivalents of carbon (Cailliot, 1846a, 1847).

### *Pimaric acid*

According to Cailliot although Laurent had discovered pimaric acid in the turpentine and galipot of the maritime pine, the acid had not been studied in detail (Laurent, 1848). Different chemists had assigned to its melting point very different values, varying from 125° to 165 °C, probably due to having been measured on different varieties and degrees of purity of the galipot (Cailliot, 1874).

Cailliot conducted his experiments on a fresh sample of galipot, carefully selected. He first washed it with alcohol at room temperature and then at 60 °C with twice its weight of alcohol of 85%. The alcoholic extract, rapidly cooled, deposited a grainy acid material, which melted at 125 °C and had all the properties given by Laurent: it deposited as rigid plates of curvilinear contour, which changed afterwards into octagonal levorotary plates. The rotary power decreased strongly with concentration, it was  $-92.7^\circ$  for an alcoholic solution containing 0.058 g of active material, to  $-78.6^\circ$  when the concentration increased to 0.248 g. Repeated crystallizations from alcohol did not change the melting point and rotary power of the acid, but if the solution was made highly concentrated and allowed to cool slowly, the crystals deposited had a higher melting point and a lower rotary power. This result probably explained the difference in melting point reported by previous researchers. Upon heating a solution of levorotary pimaric acid in closed tubes, in an atmosphere of hydrogen, the rotatory power decreased to zero and then became positive. The results suggested that the boiling the solution of pimaric acid resulted in the formation of three acids: (1) A dextrorotary acid ( $+56^\circ$ ), melting above 200 °C and crystallizing in rectangular plates; (2) a levorotary acid ( $-66^\circ$ ), melting at 145 °C, more soluble in alcohol than the dextro variety, and identical with the pyromaric acid which Laurent obtained by distilling pimaric acid under vacuum; and (3) an intermediate product containing variable proportions of the dextro and pyromaric acids, and another slightly levo acid whose presence was shown by its reaction with NaOH (Cailliot, 1874).

This change of the rotating power of pimaric acid could also be produced by its simple solution in solvents such as ethyl acetate, chloroform, benzene, essence of turpentine, and

particularly, in carbon disulfide. For example, dissolving pimaric acid having a rotatory power of  $-92.7^\circ$  in carbon disulfide decreased the rotatory power to  $-11.5^\circ$ , but after evaporation of the solvent and solution in alcohol, the acid had a power of only  $-37^\circ$ . The acid so altered by carbon disulfide furnished immediately the dextropimaric and pyromaric acids (Cailliot, 1874).

Pimaric acid was sparingly soluble in cold NaOH but much more in the warm reagent. Upon cooling the solution separated into two parts, one containing a crystalline mixture of sodium dextropimarate and sodium pyromarate, the other a non-crystallizable mother liquor from which it was possible to separate a weakly levorotatory acid (Cailliot, 1874).

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