

# HENRI-FRANÇOIS GAULTIER DE CLAUBRY

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**RESUMEN.** Henri-François Gaultier de Claubry (1792-1878) was a French pharmacist and chemist who is well-known for his discovery of starch as a reagent for iodine (together with Colin), the synthesis of organic esters and alkyl halides, the presence of iodine in a variety of algae, the nature of amyl alcohol, the separation of inulin, dyes, methods for the analysis of poisons, and the use of chlorides for disinfection purposes.

**ABSTRACT.** Henri-François Gaultier de Claubry (1792-1878) fue un farmacéutico químico francés, conocido especialmente por haber descubierto el almidón como reactivo para el yodo (junto con Colin), la síntesis of ésteres orgánicos y haluros alquílicos, la separación de la inulina, la naturaleza del alcohol amílico, colorantes, métodos analíticos para venenos y el uso del cloruros como desinfectantes.

## INTRODUCCIÓN

### Life and career<sup>1,2,3</sup>

Henri-François Gaultier de Claubry (Fig. 1) was born in Paris on July 21, 1792, the son of Charles Gaultier de Claubry (1757-1821), a well-known physician.



**Fig. 1.** Henri-François Gaultier de Claubry (1792-1878), from BIU Santé, Paris

At the age of 14 he began his studies of pharmacy working in the pharmacies de Pelletier and de Boudet and the Hôpital de la Charité. Three years later he began working in the laboratory of Joseph-Louis Gay-Lussac (1778-1850) at the l'École Polytechnique and in 1812 he transferred to the Faculté des Sciences de Paris to serve, without a formal appointment, as préparateur of the course given by Louis-Jacques Thenard (1777-1857). In 1818 he was appointed répétiteur at the École Polytechnique, a position he resigned in 1824 when he received his doctorate after successfully defending in 1815 a thesis about the existence of iodine in algae<sup>4</sup> (and in 1824 another about the classification of metals).<sup>5</sup> His position at École was assigned to Jean-Baptiste André Dumas (1800-1884). During this period he also taught physics at the Collège Stanislas the Athénée Royal, the Société des Bonnes Lettres, and the Société des Bonnes Etudes. In 1832 he received his degree in pharmacy after defending a thesis about the conversion of alcohol into acetic acid.<sup>6</sup> In 1835 the King Louis Philippe appointed him adjunct professor for the chair of chemistry at the École

de Pharmacie and at the École Polytechnique. He held the chair until 1859 when he was appointed professor of Toxicology at the École Supérieure de Pharmacie, replacing Joseph Bienaimé Caventou (1795-1877). His position at the École Supérieure de Pharmacie was assigned to Jules Bouisi (1822-1886).

In 1825 Gaultier de Claubry was elected adjunct member of the Conseil d'Hygiène of the Department of the Seine, replacing the surgeon Baron Guillaume Dupuytren (1777-1835), and in 1828 he was promoted to full member. He kept this position until 1859. He 1848 he was elected member of the Académie de Médecine and in the following years officer of the Légion d'Honneur, chevalier of the l'Ordre des Saints Maurice and Lazare of Italy.

Gaultier de Claubry passed away in Paris, on July 4, 1878.

### SCIENTIFIC WORK

Gaultier de Claubry wrote more than 70 papers, booklets, and books in the areas of organic and inorganic chemistry, toxicology, public health, medicine, and meteorology. He also published a booklet describing his research activities and results, as customary for candidates for membership in the Académie de Médecine.<sup>7</sup> He 1812 he translated to French the famous chemistry book of Henry Williams (1774-1836) *Elements of Experimental Chemistry*, and collected in a book Gay-Lussac's lessons of the chemistry.<sup>8,9</sup>

In addition to the subjects discussed below, Gaultier de Claubry studied the stones formed in the kidneys,<sup>10,11</sup> gallic acid,<sup>12</sup> extraction and use of bone gelatin,<sup>13</sup> the dyes present in madder,<sup>14</sup> influence of cokes in the formation of cast iron,<sup>15</sup> toxicology,<sup>16</sup> dangers of using phosphorus in matches,<sup>17</sup> separation of digitalin by means of dialysis,<sup>18</sup> etc.

### Iodine

Bernard Courtois (1777-1838), a Parisian manufacturer of saltpeter, discovered iodine in 1811<sup>19</sup>, an event that prompted an intensive research activity, particularly by Gay-Lussac, Humphry Davy (1778-1829), and Louis Nicolas Vauquelin (1763-1829).<sup>20-22</sup> All the initial research activity was devoted to determine the properties of the new element and its inorganic combinations. For these reasons Jean-Jacques Colin (1784-1865) and Gaultier de Claubry thought it would be interesting to determine the action exerted by iodine on vegetable and animal substances.<sup>23</sup> In the first part of their memoir they indicated they would describe their results using the three-tier classification of vegetable and animal substances suggested by Gay-Lussac and Thenard<sup>24</sup>: (1) substances composed of carbon, hydrogen, and oxygen, in the ratio they are present in water plus the excess oxygen (that is, the acids); (2) substances composed of carbon, hydrogen, and oxygen, in the ratio they are present in water, that is, sugar, gums, starch, etc. (carbohydrates). This category also included animal substances containing nitrogen and hydrogen in the ratio present in ammonia (albumin, gelatin, fibrin, etc.); and (3) substances similar as those in the previous category but containing an excess of hydrogen (oils, camphors, etc.).<sup>23</sup>

Colin and Gaultier de Claubry found that at room temperature substances of the first group did not react with iodine, but in the presence of boiling water iodine vapor was released and the resulting solution contained the corresponding vegetable acid. Heating a dry mixture of iodine and the vegetable substance resulted in the formation of abundant vapors of iodine and a solution containing a large amount of iodohydric acid (HI). Substances of the second group behaved differently, they reacted with iodine at room temperature yielding colored compounds; boiling water was able to separate iodine vapors only when it was at 100°C or the iodine was present in large excess. No iodohydric acid was formed and the iodine seemed to combine with the vegetable substance without decomposition. Heating to the temperature of decomposition of the vegetable matter resulted in the formation of a large amount of vapors of HI. In the presence of water, substances of the third category reacted with iodine producing HI, which could be separated by water washes. Animal substances presented the same behavior.<sup>23</sup>

The second part of the memory was devoted to a detailed description of the action of iodine on substances of the second group, particularly starch.<sup>23</sup> Colin and Gaultier de Claubry noted that mixing dry starch with dry iodine led to the immediate coloring of starch from blue to black, depending on its proportion in the mixture. This phenomenon was observed with starch of several origins, for example, from potatoes, salep, and the mucilage of the roots of marshmallow. The coloration disappeared only when the mixture was heated to the temperature of decomposition of the vegetable matter: HI vapors formed mixed with the product of the decomposition of the organic matter. The compound of iodine and starch was only slightly affected by water at room temperature; the blue or black compounds dissolved easily upon agitation; in the first case the solution was colored blue, in the second it was colorless. In the latter case, the color reappeared on addition of nitric acid, concentrated sulfuric acid, or an aqueous solution of chlorine. The solution of the compound was decomposed by sulfur dioxide producing HI and sulfuric acid and precipitating the starch. Color changes were also observed with hydrogen sulfide, chlorine, KOH, NaOH, ammonia, sodium or potassium bicarbonate, alcohol, etc. From the results of these experiments Colin and Gaultier de Claubry concluded that starch was an extremely sensitive reagent for detecting the presence of iodine.<sup>23</sup>

Gaultier de Claubry also searched for iodine in seawater and in several varieties of fucus, the algae used for producing sodium carbonate and fertilizers.<sup>4</sup> In 1815 Edmée Bouillon Lagrange (1764-1844) and Heinrich August von Vogel (1778-1867) analyzed the seawaters of France and reported they contained magnesium and sodium chloride, calcium and magnesium sulfate, and calcium and magnesium bicarbonate.<sup>25</sup> Gaultier de Claubry made a

more detailed analysis of seawater samples taken from the English Channel near Fécamp and Le Havre. The samples were first concentrated and then treated with a variety of reagents, among them, silver nitrate, barium nitrate, sulfuric acid, chlorine, mercuric chloride, bismuth nitrate, starch, etc. The starch did not change its color even in the presence of sulfuric acid. The samples were then evaporated to dryness and the residue treated with the same reagents. All the results indicated that these waters did not contain iodine.<sup>4</sup>

Gaultier de Claubry collected from the same geographical region a large number of algae belonging to the Ulvæ, Kelp, and Ceramium families, among them, ulva saccharina, ulva digitata, fucus saccharinus, fucus digitatus, fucus vesiculosus, fucus serratus, fucus siliquosus, ceramium filum, and fucus filum. All this material was subjected to the same series of treatment, which Gaultier de Claubry described in detail for fucus saccharinus: the alga was cut in small pieces, extracted with boiling water, and the solid residue and solution treated with a large number of reagents (e.g. litmus paper, silver nitrate, lead acetate, ammonium oxalate, nutgall infusion, alkali hydroxides, chlorine, starch, sulfuric acid, alcohol, etc.). The results of these tests, particularly with starch, clearly indicated the presence of iodine (as potassium iodide) in fucus saccharinus, fucus digitatus, fucus vesiculosus, fucus serratus, fucus siliquosus, and fucus filum. Fucus saccharinus had the highest content of iodine.<sup>4</sup>

In another publication Gaultier de Claubry showed that an alcoholic solution of iodine was appropriate for the dosage of tin in the presence of other metals.<sup>26</sup>

### Classification of minerals

As explained before, one of Gaultier de Claubry's doctoral theses was related to a formal classification of minerals.<sup>5</sup> According to him, the methods for classifying minerals could be divided into three groups: (1) those based on external characters, for example, Jean-Baptiste Romé de l'Isle (1736-1790) claimed that using this criterion the apparently numerous forms shown by minerals could actually be reduced to a very limited number of simple ones; (2) those based on external characters and chemical nature; Jean-René Just Haüy (1743-1822) had adopted this type of classification using crystallography and chemical composition as the identifying elements; and (3) those based only on the chemical nature; for example, Jöns Jacob Berzelius (1779-1848) had organized minerals on the basis chemical analysis and the law of definite proportions, without any consideration to their external form.

The main objective of Gaultier de Claubry's work was to illustrate the many shortcomings presented by Berzelius's procedure. This he did by comparing the information available about the analysis of silica, a series of silicate minerals, Gahnite, Aker spinel, pyroxenes, micas, feldspars, Tremolites, etc.<sup>5</sup>

Haüy's method allowed an easy classification of saline substances using as base the corresponding metallic oxides, but not so when trying to organize the alkaline earth substances, which presented a wide variety in their composition and shape and some did not crystallize. For this situation it had been necessary to partially complement the classification system with chemical information. The most serious objection against Berzelius's system was the uncertainty regarding the chemical analysis of alkaline earth oxides, particularly silica. These analyses had not been done directly, the relative proportions of silicon and oxygen had been guessed by comparison with other oxides. Thus Friedrich Stromeyer (1776-1835) had used his analytical results about alloys of calcium and iron to deduce that silica contained, by weight, 46.0069% silicon and 53.9931% oxygen. Berzelius had made two chemical analysis of silica and obtained the values 49.641 and 49.716% for the silicon and 50.359 and 50.284% for oxygen (average 50.321%). Berzelius had also tried to determine the value of the atomic mass of silicon by decomposing fluosilic acid with water, or by absorption of the gas in boric acid. The results had been too different to reach an acceptable value. In another failed attempt he had melted alumina with silica and potassium bicarbonate, decomposing the product with water, treating the residue with HCl, and adding ammonia to the resulting liquor. Chemical analysis of the different fractions had allowed him to determine the composition of the pertinent alkaline earth matter. Unfortunately, this method required a precise knowledge of silica, which was not available. Small deviations in the assumed calculations amplified significantly when calculating the composition of the product of the above reaction. Although the law of definite proportions was appropriate for reactions that occurred in a certain way, it was questionable if the results of a chemical analysis indicated the true composition of a mineral; it was perfectly possible to combine the amounts of the oxides of calcium silicon, magnesium, etc. in several proportions, without violating the law. Gaultier de Claubry illustrated this point with garnet. According to Berzelius's classification this mineral was divided in the following form: family of aluminum: oriental garnet, Almadine, Hisingerite, Brodbho garnet, and de Finbo; family of magnesium, Syrian garnet; family of calcium, black garnet of Swappara, and Thuring garnet, Melanite, Aplome, Danemore garnet, and Grossular garnet.<sup>5</sup>

Berzelius also proved that silicon behaved in many cases as an acid, which combined with oxides, particularly those of alkaline earths, to form a large number of compounds (which he named silicates). These silicates were not only very difficult to analyze, they were also very difficult to classify under his scheme. In addition, silica seemed to combine with a given oxide in many proportions.

After reporting the inconsistencies present in the analysis of many minerals, Gaultier de Claubry concluded it was possible to improve Berzelius's procedure by using as a basis the *acid group* instead of the metal oxide, as commonly done. This modification would give place to a series of families, different from the ones used actually, for example,

silicates, aluminates, etc. A good example was again garnet. Instead of dividing the study of this substance in the multitude of different sections listed above, all of them could be brought together under the same name: aluminum silicates, iron silicates, calcium silicates, etc. (that is, the salts of a given acid with different oxides).<sup>5</sup>

### **Inulin**

In 1804 Valentin Rose (1762-1807) reported that the root of elecampane (*Inula helenium*) contained "a white material appearing very much like starch, but differing from it both in its principles and in its manner of action with other substances".<sup>27</sup> Rose found that after boiling the roots in water and leaving the decoction stand for several hours, a white powder precipitated, which looked very much like starch but differed from it both in its principles and in its manner of action with other substances. This substance was soluble in cold water but readily soluble in boiling water producing a not quite transparent mucilaginous liquid. After some hours most of the solute re-precipitated as a compact white powder; addition of alcohol produced the same effect.

Rose subjected the material to series of comparative examinations with a gum (Arabic) and with common starch. For example, addition of alcohol to an aqueous solution of the powder resulted in the re-precipitation of most of the solute; while a solution of gum Arabic produced a milky solution and no precipitate. The white powder in contact with burning coal melted like sugar and evaporated giving off a white smoke smelling like burning sugar; starch emitted a similar smoke but did not melt while Arabic gum hardly smoked. When the powder was heated over charcoal in an iron spoon, it first melted and smoked as before and then burned with a bright flame, leaving a very small amount of residue. Starch under the same circumstances did not melt and took a much longer time before it burned; gum Arabic sparkled without burning and left a great amount of coal, which readily turned into grayish ashes. When treated with nitric acid Arabic gum generated a large amount of saccholactic acid, starch yielded fatty matter, and the white powder produced only malic and oxalic acids. Rose believed these results indicated that the material he had discovered was neither starch or gum but stood between the two.<sup>27</sup>

According to Gaultier de Claubry this new material had no been subject to further examination although some chemists had speculated about its possible nature. One of them, Thomas Thomson (1773-1852), had named it describe *inulin*.<sup>28,29</sup> Gaultier de Claubry repeated Rose's experiments, confirmed most of his results and added more information showing that inulin was not gum or starch. Thus, at 60°C, inulin dissolved four or five times its weight of water without jelling like starch; on evaporation the solution became viscous but not gelatinous. On cooling it deposited most of the solute, accompanied by a large amount of water. With iodine it formed a greenish-yellow compound, which easily and rapidly decomposed partially. The remaining inulin was slightly colored yellow and retained a small portion of iodine. Aqueous solutions of KOH and HCl rendered starch gelatinous but dissolved inulin without giving any jelly; addition of concentrated sulfuric acid precipitated the inulin. Inulin dissolved in concentrated sulfuric acid producing a solution colored brown; the dissolved inulin was precipitated by ammonia but not by water or alcohol. Inulin dissolved in cold nitric acid yielding a slightly yellow solution. Inulin heated with nitric acid decomposed into malic, oxalic, and acetic acids. An aqueous solution of inulin produced a white precipitate with baryta water and a grey precipitate with nutgall infusion; the solution was not precipitated by limewater and metallic salts. All these properties clearly indicated inulin was a particular material, not to be confounded with any known vegetable substance.<sup>29</sup>

To obtain inulin in a pure state Gaultier de Claubry recommended boiling the roots of elecampane in a sufficiently large quantity of water; followed by filtration, evaporation to the consistence of an extract, and addition of cold water. The precipitated inulin should then be filtered, washed repeatedly with cold water, and dried.<sup>29</sup>

### **Mode of Action of Disinfecting Chloride**

In 1824 Joseph-Louis Gay-Lussac (1778-1850) published a set of detailed instructions about his procedure for determining the purity of calcium chloride and its chlorine content, and the design of an instrument (chlorometer) to be used for this purpose.<sup>30</sup> The procedure was based on the ability of chlorine (as a gas or as aqueous solution) of destroying vegetable colors. Chlorine was easily transported and sold in several "fixed forms", for example, combined with sodium hydroxide or potassium hydroxide (*eau de javelle*), or with calcium hydroxide (calcium chloride oxygenated, calcium hydroxide chloride, lime chloride). The amount of chlorine combined with water and a base was usually determined using the procedure developed by François Antoine Henri Descroizilles (1751-1825), founded on the bleaching of indigo by chlorine.<sup>31</sup> These alkalis chlorides had also been used in large amounts as disinfectants during the cleaning of public water mains such as the sewage of Amelot and the Saint-Martin canal, as a safety measure for the workers to avoid their suffocation by the gases. According to Gay-Lussac, the purification effect of these compounds was as result of the absorption of the carbon dioxide present in the air on in the miasmas: An alkali carbonate gradually formed with the simultaneous release of free chlorine into the atmosphere.

Gaultier de Claubry conducted a series of experiments to verify the correctness of Gay-Lussac's hypothesis.<sup>32</sup> An aqueous solution of well-saturated calcium chloride was treated with a stream of CO<sub>2</sub>; as a result chlorine was quickly disengaged and after three hours or more, the whole was expelled. The resulting liquor had no bleaching powers, even on litmus paper; calcium carbonate had been formed and precipitated, except for a small portion dissolved by the

excess of CO<sub>2</sub>. In another experiment air was first passed slowly through a saturated solution of caustic potash and then through a solution of the lime chloride: no chlorine was liberated and no other effect was observed. Sodium chloride was equally decomposed by CO<sub>2</sub>, only more slowly in consequence of the solubility of the salt produced. A sample of calcium chloride was analyzed for chloride and found to contain exactly the same quantity before and after decomposition by the CO<sub>2</sub>. Gaultier de Claubry wrote that a filtered solution of calcium chloride, which had been exposed to air for two months, showed no traces of chlorine; it did not affect litmus and its precipitate proved to be calcium carbonate. Nevertheless, a stronger solution of the same chloride showed no change after a two-month exposure to air. Additional experiments involved (a) passing air through blood, which had been left to putrefy for eight days and had a intolerable odor, followed by streaming through a solution of calcium chloride. In this situation calcium was precipitated and the air rendered odorless and completely purified; (b) the same fetid air was passed through a solution of KOH before it arrived at the chloride solution. In this case the latter had no effect on the air, which retained its unbearable odor.<sup>32</sup>

Gaultier de Claubry believed that the results of his experiments proved clearly the correctness of Gay-Lussacs's explanation, as well as why using chlorides as disinfecting agents was better than fumigation with chlorine: The CO<sub>2</sub> in the air, arising from the decomposition of animal matter, slowly liberated the chlorine from its combination and made it less susceptible of affecting the animal economy while readily decomposing putrid miasma. The procedure was therefore, identical with a true fumigation by chlorine, only less violent than those made directly by the gas, and persisting for a longer time.<sup>32</sup>

### Orchil

Lichens had long been used as the source of dyes of different colors. In 1812 Cocq described the general characteristics of these lichens and the various dyes they provided [1].<sup>33</sup> In 1829 Pierre Jean Robiquet (1780-1840) reported experimental evidence proving the lichens of the *Roccella* and *Lecanora* genres (orchella weeds) contained substances, which under the influence of different reagents transformed into dyes of different colors.<sup>34</sup> For example, orchil (*Roccella tinctoria*) contained a colorless substance, which under the combined influence of ammonia and air transformed into a dye having a beautiful violet color. Robiquet developed an efficient extraction process based on successive macerations of the lichen with concentrated alcohol, followed by distillation of the extract to eliminate the solvent, extraction of the residue with ether, purification by solution in hot alcohol and recrystallization. Selective extraction of the residue allowed separating it into two different substances, a white one (*variolin*, variolarin) and *orcin* [3,5-dihydroxytoluene, C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)(OH)<sub>2</sub>], also white and having a sweet flavor. Orcin, exposed successively to the action of ammonia (or putrefied urine) and air lost its sweet flavor and took on a dark red color (Robiquet named this pigment *orcein*), which in aqueous solution yielded a red crimson tincture similar to the one produced from orchil.<sup>34</sup>

In spite of all the publications about orchil, it was yet impossible to describe the true state of this substance in the lichen.<sup>35</sup> The product sold under the name orchil was actually a mixture of several active substances, which reacted differently to a given reagent; their proportion and nature provided a group of dyes appropriate for application in the dyeing industry. Orchella weeds contained only 10 to 12% of their weight of coloring dyes. In 1848 John Stenhouse (1809-1880) used calcium hydroxide to separate the coloring principles contained in orchil.<sup>36</sup> He claimed that the material that generated orchil under the combined influence of ammonia and air was easily separated by macerating the finely cut lichen with limewater, followed by neutralization with HCl or acetic acid. Gaultier de Claubry believed that Stenhouse's procedure was appropriate only if the maceration time was very short; otherwise the result was unpredictable: The neutralization step resulted in the precipitation of all the coloring materials or in their remaining in solution. The latter result cancelled all the advantages provided by calcium hydroxide. Gaultier de Claubry justified his claim by reporting the results obtained when a mixture of 100 g of lichen orchella mixed with 600 of limewater containing 30 g of calcium hydroxide were left to stand for lengths of time varying between 1 to 46 hours, followed by separation of the solid and liquid phase, and observation of their respective colors. The results indicated clearly that depending on the time of the experiment, it was possible to obtain all the coloring material in one or the other phase. It was also found that water alone produced a similar effect, although more slowly: A short time of contact left all the coloring material in the solid phase; a longer one transferred them completely to the liquid phase.<sup>35</sup>

Additional experiments showed that if instead of operating at room temperature the liquid was brought to boiling for only three to four minutes, the acid separated only a brown matter, which did not convert to orchil when treated with ammonia. Substitution of limewater by different soluble salts (e.g. sodium, potassium, or ammonia phosphate, borax, sodium or potassium carbonate, etc.) resulted in a faster transformation of the colorable material. With potassium, sodium, or barium hydroxide, it was even faster. All these results justified the original claim that the coloring matters present in the lichen reacted in a different way with several reagents.<sup>35</sup>

### Acetification

The French Society of Pharmacie, as other French scientific organizations, called every so often for a national competition to solve a problem in theoretical chemistry and/or a practical problem of the manufacturing industry. In

1826 the candidates were required to answer the following questions: (1) Determine the essential phenomena that accompany the transformation of organic substances into acetic acid by fermentation; (2) determine if the formation of acetic acid is always preceded by the formation of alcohol, in the same manner as the formation of sugar precedes the formation of alcohol in the alcoholic fermentation; (3) determine the substances which can serve as ferments (enzymes) in the acetic fermentation, and their essential characteristics; (4) determine the influence of air on the acid fermentation; and if it was indispensable, how did it act; and (5) establish a theory of the acid fermentation, in harmony with all the facts observed.

In 1827 the competition was declared desert because none of the memoirs submitted satisfied the conditions of the contest. Consequently, the Society of Pharmacy decided to restrict the contest to the question of acetification of vinous liquors in general. The contestants were now required to answer the following questions: (1) Describe in precise terms the condition that determine the transformation of alcohol into acetic acid; and (2) describe the phenomena that accompany this transformation and all the resulting products. The closing date of the competition was October 1, 1831.<sup>37</sup>

Only four contributions were received; the Prize Committee decided that the best were those of Apollinaire Bouchardat (1809-1886) and Gaultier de Claubry, and awarded each a medal worth 400 francs. Interesting enough, both memoirs answered all the questions asked in the original competition.<sup>37</sup>

In his memoir [2], Gaultier de Claubry wrote that the questions posted in the presence competition were far from being as interesting as those in the original event. For this reason he had extended his contribution to provide an answer to the five original questions in an order he believed was more logical: 4, 2, 1, 3, and 5. Regarding the influence of air on the acid fermentation, he wrote it was a known fact that fermentable liquors transformed, more or less faster, into vinegar when they were kept in vessels having a hole in their cover. The flow of the air going into the vessel was clearly heard and this fact indicated that part of the air was being absorbed. Saussure believed that oxygen was not absorbed and that an equal volume of CO<sub>2</sub> had replaced it; the absorption of the latter gave place to the decrease in pressure observed.<sup>38</sup> Gaultier de Claubry carried on a series of experiments to prove that alcohol alone did not transform into acetic acid, to do it required the presence of another organic substance able to transform a small part of alcohol into the acid; from there on the reaction continued alone in the presence of air. He also tested the influence of air on other substances that produced acetic acid. For example, he found that very pure gum dissolved in water did not become acid, but when the solution contained a small amount of mucilage, gluten, or yeast, it promptly acidified if in contact with air. Milk behaved in a different manner, it acidified in the absence or in contact with air. Gaultier de Claubry stated that milk, heated to a temperature between 25 °C and 40 °C under vacuum, soured considerably with release of an amount of gas equivalent to about 40% of the volume of the liquid. Other experiments conducted with an aqueous solution of gluten, gelatin, and muscular tissue led to the same conclusions: (a) the action of oxygen on alcohol converted it into acetic acid; (b) alcoholic liquors did not acidify under vacuum; (c) the acidification of alcohol did not generate CO<sub>2</sub>; (d) sugar solutions turned first into alcohol and then into acetic acid, except when in the absence of air (unless they contained vegetable albumin or purified animal matter); and (f) gum, in contact with gluten or yeast formed acetic acid without producing alcohol, by absorbing oxygen from the air.<sup>37</sup>

Gaultier de Claubry contacted a large number of fermentable vegetable infusions (e.g., gum treated with yeast, mauve, licorice, the juices of potato, carrot, onion, juice, etc., honey, etc.) with air, at room temperature and for a long time, and tested the resulting liquids for the presence of alcohol. In most cases the result was negative. All these facts indicated that acetification could take place without a sensible production of alcohol. All the substances that produced acid without previously converting into alcohol seemed to go through the same chain of events: absorption of oxygen, production of small amounts of CO<sub>2</sub>, and successive disappearance of the original substance.<sup>37</sup>

Gaultier de Claubry presented a shorter version of his memoir to the École de Pharmacie as part of the requisites for the degree of pharmacist. The thesis included details (in Latin) on the preparation of 8 compositions based on acetic acid.<sup>6</sup>

### Esterification

At the time of Gaultier de Claubry the term ether was used in a very general form; it included not only ethers (in the modern chemical nomenclature), but also esters and alkyl halides. In a paper published in 1842 Gaultier de Claubry reported that only a few inorganic acids and acetic acid were known to transform alcohol into ether (ester). The formation of the latter was assumed to occur by a succession of actions, the number of which depended on the rapidity with which the operation was conducted. There was little difference between the glacial acid and the acid containing a larger proportion of water. Gaultier de Claubry thought that a possible explanation for the inability for producing esters of other acids was due to the fact that the reaction was executed by distilling a *mixture* of the reagents. He went on to try a different procedure in which the acid was heated just to the point at which it began to decompose, and then the alcohol was added drop-wise. Gaultier de Claubry believed that in this situation, the acid having lost its water and being in excess in proportion to the alcohol, would lead to the formation of the ester. His results indicated that several acids behaved as expected. For example, heating oxalic acid in a multi-neck vessel just to the point at which it begun to release white vapors of the acid with only one atom of water, most of the alcohol,

after being dropped in, converted into ester, which distilled over with a portion of unaltered alcohol. This procedure allowed preparing a large amount of oxalic ether (ethyl oxalate). Similar results were obtained with benzoic, succinic, and citric acids. Gaultier de Claubry wrote that he had not been yet to determined whether the ether obtained from citric acid was the citric, itaconic, or aconitic one. The results with mucic, tartaric, gallic, tannic, and fatty acids were inconclusive, as those of the reaction with wood spirit (methanol); he did not know if this was due to the higher volatility of the alcohol or of its being etherified with more difficulty.<sup>39</sup>

### **Amyl alcohol**

In 1785 Carl Wilhelm Scheele (1742-1786) observed that the distillation of fermented potatoes was accompanied by the production of a volatile oil (fusel oil). In 1834 Dumas determined this oil contained by weight 68.6% carbon, 13.4% hydrogen, and 18.0% oxygen, corresponding to the formula  $C_{10}H_{12}O$ ; <sup>40</sup> in 1838 Auguste Cahours (1813-1891) recognized oil of potatoes was an alcohol, which he named *amyl alcohol*.<sup>41</sup>

In 1842, Robert de Many, an alcohol distiller from Saint-Quentin, provided Gaultier de Claubry with an essence he had separated during the distillation of the products obtained from the fermentation of beetroot molasses. This liquid was denser than molasses and had a disagreeable acrid taste and penetrating odor. Gaultier de Claubry purified the product and recognized that it was identical with the oil obtained by distillation of fermented potatoes. He treated the oil with sulfuric acid and separated by distillation four different fractions: (1) a colorless fluid of a strong bitter taste and penetrating odor, boiling at 96°C, and soluble in sulfuric acid. Gaultier de Claubry believed that this fraction was the aldehyde of the amyl series; (2) a colorless and tasteless fluid, having a pleasant ethereal odor, boiling at 170°C, soluble in sulfuric acid, which colored it red. This liquid was assumed to be the ether of the series; (3) a fluid of unpleasant odor, boiling at 160°C, insoluble in sulfuric acid, and composed only of carbon and hydrogen. Gaultier de Claubry assumed it was amylene; and (4) a small quantity of fluid of ethereal odor and strong but not bitter taste, probably composed of a mixture of unidentified components.<sup>42</sup>

### ***Analysis of poisons by electrochemical precipitation of the metals***

Gaultier de Claubry wrote that in spite all the progress done in the analytical procedures used in legal medicine for identifying organic poisons, much remained to be done when the poisons were metallic. In a memoir on the subject he first discussed the use of organic acids (e.g. HCl, nitric acid, and sulfuric acid, alone or in a mixture) for this purpose and all the disadvantages they presented for identifying metals in the presence of body fluids or tissues. He then wrote that his practical experience on the subject had led him to develop a method for precipitating all these poisons in one stage using an electric current:<sup>43,44</sup> The organic matter was first treated with strong fuming hydrochloric acid and then heated gently while adding nitric acid in small portions (aqua regia). This operation resulted in the total destruction of the organic matter with the exception of the fatty substances it contained. The resulting transparent and almost colorless liquid was separated from the fatty matters and the latter washed several times with distilled water; the several washings were added to the main bulk of the liquid. According to Gaultier de Claubry this operation was applicable with little loss to most of the organic matter analyzed in toxicological investigations: the stomach, intestines, liver, vomits, excrements, blood, urine, wine, milk, the earth of graveyards, etc. When searching for the presence of arsenic (a volatile matter) it was preferable to conduct the process in a retort provided with a receiver, and the distilled liquid added to the rest. The excess acid was then eliminated by slow evaporation and two platinum strips introduced into it to build a constant current battery. When no zinc was present in the tested sample, it was possible to replace one of the platinum strips by another made of zinc (positive pole). Normally, after no more than eight or nine hours of operation the negative pole (platinum) became covered with a crust of the metal or metals contained in the solution. It was now withdrawn, washed with distilled water, and then digested in cold or hot nitric acid. The resulting solution was tested for all the suspected metals, such as arsenic, antimony, lead, copper, zinc, etc. This procedure detected extremely small quantities of all the metals except silver, which rarely occurred in cases of poisoning. It also had the advantage of precipitating all the metals at once, eliminating the need of carrying specific searches for each or any of them.

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