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Victor Dessaignes

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RESUMEN. Víctor Dessaignes (1800-1885), un abogado y médico Francés, convertido en químico, realizó investigaciones en química orgánica y fisiológica A su crédito es posible mencionar el descubrimiento del ácido hipúrico y su desdoblamiento en ácido benzoico y glicina, la síntesis del ácido aspártico a partir del amonio dimalato, la conversión del ácido tartárico en su racemato; el descubrimiento de la propilamina en *chenopodium vulvaria* y del ácido fumárico en los hongos, así como la naturaleza del quercitol y la síntesis de un gran número de amidas.

ABSTRACT. Victor Dessaignes (1800-1885), a French lawyer and physician, turned chemist, carried on researches in organic chemistry and physiology. To his credit it is possible to mention the discovery of hippuric acid and its splitting into benzoic acid and glycine, the synthesis of asparagine from ammonium dimalate, the conversion of tartaric acid into its racemic isomer; the discovery of propylamine in *chenobium vulvaria* and of fumaric acid in mushrooms, the nature of quercitol, and the synthesis of a large number of amides.

Life and career[1,3]

The only detailed information about the life and work of Victor Dessaignes are three papers published by his great grandson Alban Ribemont–Dessaignes (1847-1940), who at sometime decided to add to his name that of his mother.[1,3] The first paper includes a biography of the great grandfather, and the third, reprints of every paper published by the grandfather.

Victor Dessaignes, the third son of Jean-Philibert Dessaignes and Emilie-Françoise Renou, was born in *Vendôme* on December 20, 1800, at the *College de Vendee*, transformed by his father and another Oratorian, his uncle Lazare-François Mareschal (1770-1831), into a private boarding school. His brothers were Jean Octave (1795-1883), Léon (1796-1863), and Philibert (1805-1898). Jean-Philibert Dessaignes (1762-1832) was interested in physical sciences, particularly in luminescence phenomena; he believed that different phenomena, such as heat, light, magnetism, and electricity, were external manifestations of the same ethereal fluid, provoked by different movements. In 1809, his memoir was awarded the 1807 Grand Prize established by the class of mathematics and physics of the Institute de France to the best essay on the subject "Establish experimentally the relation between the different modes of phosphorescence and their reason, excluding the examination of similar phenomena observed in animals".

Victor Dessaignes carried on his basic education in his father school and then moved to Paris, where he obtained his diploma of *bachelier ès lettres* in February 1819. After graduation he began his law studies at the *Faculté de Droit de Paris*, while working as a lawyer's clerk. He received his bachelor in law diploma on December 1820 and took his oath as lawyer on November 1822. One of his friends, Alfred Donné (1801-1878), convinced him to study medicine, and so Victor registered at the *Faculté de Médicine du Paris* in 1824, where he received his diploma of *bachelier ès sciences* in 1827, and his doctorate in 1835. For his doctoral thesis he selected a subject in physiological and biological chemistry: *Les Corps Analogues par leurs Propriétés Chimiques se Ressemblent-ils par les Modifications qu'ils Impriment aux Organes des Animaux Vivants*?[4], which he defended in July 1835; his thesis was considered so impressive that the jury invented the special qualification *très parfaitement satisfait*, to qualify it.[3] After graduation he returned to Vendôme and between 1836 and 1837 taught a course on anatomy and physiology at the school directed by the Père Duchesne. He could not suffer the look of blood and hence, instead of practicing medicine, he turned to chemistry, the science he loved the most.[2,3]

The financial needs of his marriage to his cousin (1837), forced him to apply to the position of *receveur municipal* (fee collector). His young wife died in 1839 as a consequence of a fall on ice slick, a short time after giving birth to their only son.[2] Victor Dessaignes was presented several times as candidate for corresponding membership in the *Académie des Sciences*; in the third place in 1856, in the second place in 1863, and in the first place in 1869, obtaining then 35 of the 38 votes emitted [replacing Christian Friedrich Schönbein (1799-1868)]. In 1859, he was elected member of the *Société Chimique de Paris*. In 1861, he and his close friend Marcellin Berthelot (1827-1907), were awarded the Jecker Prize of the *Académie des Sciences* (a prize established in 1851 to accelerate the progress in organic chemistry). In 1861, he was nominated corresponding member of *Société des Sciences Naturelles de Cherbourg*. In 1862, he become one of the first members of the recently created *Société Archéologique* and was its treasurer between 1865-1868. In 1863, he was elected *chevalier* of the *Légion d'Honneur*, at the recommendation of *Académie des Sciences*. In 1865, he was elected foreign member of the Chemical Society of London.[1]

In December 1884, he showed the signs of bronchitis, which led to his sudden death on January 4, 1885. Marcellin Berthelot pronounce a eulogy at the *Académie des Sciences* and the *Société Chimique de Paris*, and Émilien Renou (1815-1902), at the *Société Chimique de Paris*.

Dessaignes's researches were in the area of organic chemistry. In 1845, he observed the splitting of hippuric acid into benzoic acid and glycine[5] and in 1853, he achieved the reverse reaction, the synthesis of hippuric acid.[6] From 1852 on he studied the oxidation of tartaric and malic acids, which led him to discover two new acids, tartronic (2-hydroxymalonic acid) and malonic acids.[7-12] He synthesized aspartic acid from ammonium dimalate;[13] converted malic acid into succinic acid,[14] and tartaric acid into malic acid,[11] reactions which helped establish the essential relations between many of the acids present in vegetables. He converted tartaric and paratartaric (2,3-dihydroxybutanedioic acid) acids into racemic tartaric acid.[15] He discovered the presence of propylamine in *chenopidum vulvaria;*[16] studied the nature of the sugar present in acorn[17], showed that bolic acid discovered by Henri Braconnot (1780-1855) in mushrooms was actually fumaric acid and that the fungic acid of Pompeious Alexander Bolley (1812-1870) was actually a mixture of malic and citric acids.[18] Additional work included the fermentation of succinic acid;[19] the nature of quercitol,[20] trimethylamine,[21] amides,[22] creatine and creatinine,[23] methyluramine,[24] aconitic acid,[25] etc. Together with Jules-Maria Augustin Chautard (1826-1901) he discovered the presence of *levo*-camphor in chamomile, and physalin, the bitter principle of *Physalis alkekengi*.[26,27]

Scientific contribution

Dessaignes wrote 27 articles alone or in collaboration with Chautard, all of them in the area of organic chemistry and physiology.

Quercitol **(Acorn sugar)**

In 1849, Henri Braconnot (1780-1855) reported the presence of a sugary material in the fruit of two varieties of oaks, *Quercus racemosa* and *Quercus sessiliflora*. He found that the properties of this sugar were very similar to those of lactose, the sugar present in the milk of mammals; in the same manner that vegetable casein was very similar to casein of milk. Braconnot believed that his findings pointed to an important parallel between vegetable physiology and animal physiology.[28]

According to Dessaignes, one of the most interesting discoveries of Henri Braconnot (1780-1855) was finding lactose in oak seeds,[17] although the small amount of sugar on which he had carried his experiments had not allowed him to establish the definite identity of this sugar with the one present in human milk. For this reason, and the importance of this discovery in the study of vegetable physiology, Dessaignes decided to carry on further experiments to assert the identity of the new sugar.

In his first experiments he prepared several grams of this sugar matter and from its examination he realized it was a body *sui generis,* very distinct from sugar of milk, and different in composition and characters from all known sugar bodies. Actually, it most nearly resembled mannite (today: mannitol) and dulcose (today: dulcite, galactitol).

Dessaignes found that the sugar of the acorn crystallized in very fine prisms, which remained completely transparent, when they were formed by the cooling of a weak alcoholic solution. No heat loss was observed when heated to 210 $^{\circ}$C; at 235 $^{\circ}$C it fused and released a vapor, which condensed as a slight crystalline sublimate. At this high temperature, it decomposed slightly, producing a black matter. The remainder, redissolved in water, crystallized without alteration. Treated with warm ordinary nitric acid it produced only oxalic acid, without any mixture of mucic (galactaric) acid. Crushed with concentrated sulfuric acid, it dissolved without becoming colored, and formed a copulated acid, whose calcium salt did not crystallize. Treated with a mixture of concentrated sulfuric and nitric acids, it produced a detonating body, having the appearance of a white resin, insoluble in water, soluble in hot alcohol but from which it did not crystallize, and in this respect differed from nitromannitol.[17]

Dessaignes also studied the reaction of an aqueous solution of acorn sugar with several other reagents, among them, KOH, lime, baryta, cupric acetate, a mixture of cupric sulfate and KOH, basic lead acetate, beer yeast, etc. A mixture of acorn sugar and casein, left alone for one month, did not show the presence of lactic acid, and the sugar could be recovered completely from the final product. Combustion of the sugar with cupric oxide and potassium chlorate indicated that its elementary composition was 43.60 to 43.88 % carbon, and 7.60 to 7.47 % hydrogen, which corresponded to the composition of mannitol, less the elements of water.

Dessaignes concluded that the sugar of acorn represented a distinct and well-defined chemical species, and, on this account, ought to have a name. He left to Braconnot, its discoverer, to give it one.[17] Eventually Dessaignes named acorn sugar, *quercite*, with the agreement of Braconnot.[20]

In a following paper, Dessaignes described the regeneration of mannite (mannitol) and quercite (quercitol) from their nitro derivatives. In the opening statements he wrote that the nitrogen bodies derived from the combination of nitric acid and organic substances had not been modified yet in such a way as to recover the material from which they derived. He now reported the procedure to do so with nitromannite (mannitol hexanitrate, $C_6H_8N_6O_{18}$) and nitroquercite (nitroquercitol).[20]

The reduction was carried on by treating a warm alcoholic solution of the nitro derivative with a very concentrated solution of ammonium bisulfide, saturated with hydrogen sulfide. The reaction was very neat, particularly with nitroquercite, and was accompanied by the release of a large amount of ammonia and formation of sulfur, which accumulated on the surface. The solution was evaporated to dryness on a sand-bath and then redissolved in hot water and filtered. With nitroquercite, the filtered liquid was nearly colorless. By evaporation it deposited large crystals, easily purified, which presented all the characters of the acorn sugar, and contained 43.69 % carbon and 7.71 % hydrogen (the theoretical values are 43.90 % carbon and 7.31 % hydrogen). The reaction product of nitromannitol and ammonium bisulfide was colorless (especially if the hydrosulfate employed was not concentrated), and shown to contain a considerable amount of an ammonia salt of an organic acid. The evaporated liquid yielded a crystalline mass, which on being redissolved and discolored by animal charcoal, produced by spontaneous evaporation prisms of a sweet taste, which presented the properties of pure mannitol; its elemental analysis, gave C 39.69 % carbon and 8.03 hydrogen (the theoretical values are 39.55 % carbon and 7.68 % hydrogen).[20]

Propylamine

According to Chevallier and Lassaigne, most of the vegetables, which had been analyzed thus far showed the presence of an acid. They had analyzed the composition of *Chenopodium vulvaria* (stinking goosefoot), a plant that spread a smell of rotten fish when touched, and found it contained a free alkali, which seemed to be ammonia.[29] Their results indicated that the plant produced white fumes when in contact with vapors of nitric acid. Crushing the plant with boiling water left a green precipitate and a yellow green solution, which turned blue litmus paper previously reddened by an acid. This solution released a strong smell of ammonia when treated with KOH; did not precipitate a solution of barium nitrate but produced an abundant precipitate with silver nitrate, limewater, lead acetate, chlorine, gallnut, and concentrated sulfuric and nitric acids. A large amount of the plant, distilled in the absence of water, in a water bath, yielded a milky liquor, having a smell of rotten fish stronger than that of the plant itself. Treatment of this liquor with different reagents indicated that it contained ammonium bicarbonate, which Chevallier and Lassaigne believed it was liberated by a putrefying animal matter present in the living plant.

In 1848, Thomas Anderson (1819-1874) discovered that treating codeine with alkalis, produced an oily liquid containing ammonia, which he named metacetamide;[30] a similar liquid was obtained by distillation of bone oil.[31] In 1849, Charles-Adolph Würtz (1817-1884) announced the discovery of *méthylammoniaque* (methylamide) and *éthylammoniaque* (ethylamide) ;[32] and in 1850, Theodor Wertheim (1820-1864) found that the degradation of narcotine produced an intense fishy-smelling substance, which he named oenylamine.[33] The formula of oenylamine suggested that it was the following member in the series formed by methylamine and ethylamine. In a following paper Anderson,[34] reported a more detailed study of the products of the distillation of bone oil, and wrote that he preferred changing the name of metacetamide to propylamine, in accordance with the name which was then applied to the acid with which it corresponded.

The analogy between the odor of chenopodium and that of one of the series of ammonia bases of the series discovered by Würtz, Anderson, and Wertheim, led Dessaignes to investigate the possibility that propylamine was present in stinking goosefoot in a natural state.[16] For this purpose he submitted 40 kg of the plant to many distillations, in the presence of a diluted solution of KOH, or of a solution of sodium carbonate. The products of these distillations were first neutralized with HCl, then evaporated to dryness, and then treated with concentrated alcohol, leaving a large amount of undissolved ammonium chloride. The alcoholic solution was treated with platinum chloride and the precipitate was separated by filtration, washed with alcohol, and then dissolved in a small amount of hot water. On cooling, the aqueous solution deposited large orange red crystals of a double salt of platinum and an organic base. Further crystallizations eliminated the small amount of ammonium chloroplatinate present as impurity.

Dessaignes also used an alternative method to prepare this salt free of ammonia. The impure hydrochloride, prepared as described above, was treated with gold chloride and the resulting precipitate dissolved in hot water. On cooling, the aqueous solution deposited a beautiful yellow red double salt, slightly soluble in cold water, and crystallizing as feather hairs, similar to those of ammonium chloride. The salt hydrochloride was found to be deliquescent; nevertheless, in concentrated solutions it crystallized as elongated prisms, which also crystallized by sublimation. Its aqueous solution, mixed with KOH, disengaged an ammoniacal odor accompanied by another of cod or cooked crayfish.

Dessaignes used different analytical techniques to determine that the platinum salt contained 13.93 % carbon, 3.91 % hydrogen, 5.10 % nitrogen, 40.50 % chlorine, and 37.02 % platinum, which indicated that it was propylamine chloroplatinate. Hence it was clear that propylamine and ammonia were present simultaneously in the vivant plant. It was also accompanied by a large amount of protein material, coagulable by heat.[16]

Plant principles

Chamomile

A plant principle studied by Dessaignes and Chautard, was the essential oil of chamomile (*Matricaria parthenium*).[26] They collected the plant during the flowering season of 1845 and 1846, and subjected all its parts to distillation. They reported that the oil obtained in the dry hot summer of 1846 became filled in the course of twenty-four hours with large crystalline laminæ of stearoptene (the solid part of an essential oil), while no such solid appeared in the oil collected in 1845. The distillate of the two years was united, and exposed to a temperature of 4° to 5 °C, when it deposited numerous crystals. The stearoptene was separated and then exposed to the air for several days. The mass, at first homogeneous and granulated, became firm, brittle, and assumed a crystalline appearance. The pure stearoptene had a strong odor of camphor; it melted at 175 °C and boiled at 204 °C. It was burned in the presence of cupric oxide of copper, and an analysis of the combustion gases indicated that its composition was 78.76 % carbon, 10.69 % hydrogen, and 10.69 % oxygen, a composition identical with that of the camphor of laurels.[26]

After separation of the camphor, the remaining material was dried over calcium chloride and analyzed by combustion; the results indicated 77.50 % carbon and 10.37 % hydrogen. All these results indicated clearly that the essential oil of chamomile was a mixture; it began to boil at 160 °C and then the temperature rose rapidly. The largest portion distilled between 205° and 220 °C, leaving a colored residue. On cooling sufficiently, all the portions collected between 200° and 220 °C deposited a large amount of camphor, which was separated. According to Dessaignes and Chautard, the volatile oil of chamomile most probably contained, besides camphor, a hydrocarbon of the formula C_5H_5 and an oil containing more oxygen than camphor.[26]

In this paper Dessaignes and Chautard reported also the preparation and properties of calcium dimalate, valeramide, butyric acid, and asparagine.[26]

Physalis alkekengi

On December 3, 1851, Dessaignes and Chautard reported to the *Société de Pharmacie* the results of their analysis of the plant *Physalis alkekengi* (winter berry), which was being used successfully for the treatment of intermittent fevers. Dessaignes and Chautard thought that perhaps this plant contained a febrifuge principle, which might be used as a substitute for quinine.[27]

According to Dessaignes and Chautard, every part of the alkekengi was bitter, above all the leaves, and the capsules, which enclosed the fruit. In their first experiments they extracted the leaves with alcohol and cold water; the alcoholic extract was evaporated to dryness leaving a bitter residue much colored with chlorophyll. The aqueous infusion was brown and bitter; the bitterness could be eliminated by treatment with animal charcoal, and recovered from the charcoal with boiling alcohol. Evaporation of the alcoholic extract left a yellowish brown and very bitter residue. In another experiment, the aqueous solution was first treated with KOH and then with chloroform; an almost white deposit settled after long repose. This residue was separated by filtration, washed with water, and dried to a pulverulent material, almost colorless and bitter. A chemical examination showed that it did not contain nitrogen and did behave with acids as alkaloids did; for these reason it was decided to eliminate the treatment with KOH and proceed to extract the aqueous solution directly with chloroform. The resulting bitter principle was purified by solution in warm alcohol, followed by addition of a small amount of charcoal, and precipitating the solute with cold water.[27]

According to Dessaignes and Chautard, the bitter substance, which they named *physalin*, was a light, white powder, seemingly not crystallized, with a yellowish tinge, which was impossible to remove. Its taste was weak at first, afterwards fresh bitter, and remained long in the mouth. When heated, it softened towards 180 °C, at 190 °C it was in a state of pasty fusion, and afterwards it became colored and full of bubbles. It burned without leaving a residue; it was sparingly soluble in cold water, less soluble in boiling water, very sparingly soluble in ether, very soluble in chloroform and in warm alcohol.[27]

Physalin was very little soluble in weak acids, and its solution in hydrochloric acid, evaporated to dryness, retained only traces of acidity. Heated with KOH, it did not disengage ammonia; it dissolved very readily in heated ammonia; but evaporation separated it entirely from this alkali. Treated with an ammoniated solution of lead acetate it produced a flaky yellow precipitate: elemental analysis of the latter suggested that its composition corresponded to the formula

$C_{28}H_{30}O_9 \cdot 3PbO$. According to Dessaignes and Chautard, the composition of physalin seemed to be very similar to that of cnicine, the bitter principle of the holy thistle (*Cnicus benedictus*). They ended their paper reporting that they had extracted from the red berries of the plant an acid crystallizing in fine crystals, having all the properties of citric acid.[27]

Organic acids

Hippuric acid

Dessaignes remarked that although hippuric acid had already been the subject of numerous researches; its transformations were interesting enough to suggest additional studies.[5] Julius von Liebig (1803-1883) had shown that when hippuric acid was dissolved in boiling hydrogen chloride, it crystallized on cooling without having been altered, but if the ebullition was extended for about half an hour, it decomposed, and yielded, (according to what Dessaignes had verified) a quantity of benzoic acid equal nearly to that indicated by theory.[35] The benzoic acid was separated by filtration and the filtered liquor gave by evaporation long acid nitrogenous prismatic crystals, combined with hydrogen chloride. These crystals were neutralized by sodium or lead carbonate, and after removing from the solution the chlorides of sodium or lead; fresh crystals of a very sweet and nitrogenated matter were obtained. These crystals were neutral to reagents and formed crystalline compounds with silver oxide, and nitric, sulfuric, and oxalic acids.[5]

Dessaignes promptly realized that he had obtained, by a transformation that might have been foreseen, the gelatin sugar (glycine) discovered by Henri Braconnot (1780-1855) in 1820.[36] Thus, assuming the atomic masses of carbon, hydrogen, and oxygen, were 150, 6.25, and 17.5, respectively, it was possible to write $C_{18}H_{18}N_2O_6$ - $C_{14}H_{12}O_4$ = $C_4H_6N_2O_2$; to which it was enough to add 1.5 equivalents of water to obtain the 0.5 equivalents of gelatin sugar, as suggested by Gerardus Johannes Mulder (1802-1880) and Jean-Baptiste Boussingault (1802-1887).[37,38] Dessaignes believed that it was necessary to add two equivalents of water in order to obtain $C_4H_{10}N_2O_2$, the true equivalent of gelatin sugar as already indicated by Charles-Frédéric Gerhardt (1816-1856).[39,40]

Dessaignes's results convinced him that the sweet nitrogenated matter he had obtained from hippuric acid was identical with the gelatin sugar derived from isinglass; nevertheless he thought that it was necessary to assert his assumption by an analysis of the sugar of hippuric acid. The pertinent transformation was very neat; no gas was evolved during the reaction and the only two products were benzoic acid and sugar hydrochloride. From 100 parts of dry hippuric acid Dessaignes obtained, 67.49 parts of benzoic acid and 59.08 of sugar hydrochloride (dried over sulfuric acid), for a total of 126.57.

The conversion or hippuric acid into benzoic acid was easily carried on with several other reagents. Nitric acid boiled for twenty minutes with hippuric acid, converted it into benzoic acid and nitrosaccharic acid, which crystallized in truncated tables. Nitrosaccharic acid, prepared with the sugar of isinglass, yielded exactly the same crystals. Sulfuric acid diluted with twice its volume of water converted hippuric acid into sugar and benzoic acid, without release of gas and without coloring the solution. A very concentrated solution of oxalic acid boiled for two hours with hippuric acid, converted it into benzoic acid and sugar oxalate, which crystallized in fine prisms. An excess of KOH or NaOH, boiled for half an hour with hippuric acid, converted it into an alkaline benzoate and sugar, which was obtained in the form of hydrochloride, after treating the mixture of benzoate and sugar with hydrochloric acid.

Similar results were obtained with HCl. When hippuric acid was boiled for about half an hour with HCl, it no longer crystallized on cooling, but was decomposed and afforded the quantity of benzoic acid indicated by theory. Evaporation of the filtrate yielded long prismatic crystals, acid and nitrogenated, and combined with HCl. Dessaignes separated the acid and obtained a sweet crystalline nitrogenated substance, which analyzed proved to be gelatin sugar (glycine).[5,41]

Additional work led Dessaignes to consider hippuric acid as a secondary acid with a constitution similar to that the benzoylsalicylamide synthesized by Gerhardt and Luigi Chiozza (1828-1889).[6,42]

Succinic acid

In 1806, Louis Nicolas Vauquelin (1763-1829) and Pierre Jean Robiquet (1780-1840), while inspecting the juice of asparagus, noticed the presence of some unusual crystals, which they found to be composed of carbon, hydrogen, oxygen, and nitrogen. This substance was asparagine, the first amino acid to be isolated.[43]

In 1848, Raffaele Piria (1814-1865) published a detailed analysis of asparagine and its properties.[44] His results indicated that this substance was acid enough to redden litmus paper and to displace acetic acid from its combination with copper. The resulting copper salt was insoluble in cold water, slightly soluble in warm water and very soluble in acids and in aqueous ammonia. It did not decompose when heated to 120 °C in the presence of dry air, but it did at higher temperature, releasing large amounts of ammonia. Elemental analysis of crystalline asparagine indicated that it contained 32.09 % of carbon, 6.79 % of hydrogen, 18.80 % of nitrogen, and 42.32 % of oxygen. An aqueous solution, left alone, decomposed after some time and the asparagine converted into ammonium succinate; the latter salt, under the action of oxidants such as nitric acid and chromic acid, did no reconvert into asparagine. Acids and alkalis transformed easily asparagine into aspartic acid and ammonia; pure nitric acid generated asparagine nitrate and ammonium nitrate but if the acid contained nitrous vapors (N_2O_4) a completely different reaction took place: malic acid was produced, together with a large amount of pure nitrogen gas. According to Piria, the latter result indicated that asparagine should be considered the amide of malic acid.[44]

According to Dessaignes, Piria's claim that the fermentation of asparagine transformed it into ammonium succinate could be substantiated if the same process could be applied to malic acid.[14] For this purpose he prepared an aqueous solution of calcium malate and left it by itself in a glass covered by a piece of paper. After three months, he observed that a layer of a mucilaginous substance covered the water while a large amount of calcium carbonate crystals were present at the bottom of the liquid. He separated the liquid phase by filtration and noticed that as the outside temperature increased, a mass of very fine prismatic crystals begun to precipitate. Analysis of the crystals showed that they were composed of succinic acid, which confirmed Piria's hypothesis.

In a following communication on the subject, Dessaignes proved that it was possible to prepare aspartic acid by the thermal decomposition of ammonium dimalate.[13]

Afterwards, Dessaignes reported the results of additional experiments on the production of succinic acid by the spontaneous fermentation of calcium malate. This research was considerably advanced when Liebig published a memoir on the same subject;[47] however, Dessaignes observed some additional facts, which had escaped the attention of Liebig.[19] This time he used crude casein as the agent for fermentation of aqueous solutions of calcium malate (acid and neutral), potassium malate, potassium aspartate, calcium aspartate, calcium fumarate, and calcium aconitate. The results indicated all these salts were easily converted by casein into the succinate, going through an intermediate state of ammonium aspartate. An interesting result was that fumaric, maleic, and aconitic acids transformed equally into succinic acid; this similitude of transformation was remarkable because on the one hand, calcium or sodium citrates, fermented by casein, did not transform into succinic acid, while on the other hand, the two acids derive from malic acid distinguished neatly from aconitic acid, by a different transformation. Dry distillation of neutral ammonium fumarate or maleate yielded a different substance than that produced by the dry distillation of neutral ammonium malate. Treatment of the distillate of last substance transformed it into aspartic acid; this did not occur with the distillates of ammonium neutral fumarate or maleate.[19]

In a letter to the *Académie des Sciences*, Dessaignes wrote that Charles-Frédéric Gerhardt (1816-1856) had suggested that parallel to the series of monobasic fatty acids, having the general formula $C_nH_nO_4$, it was possible to build a series of dibasic acids described by the general formula $C_nH_{n-2}O_8$.[45] Since all the acids of the two parallel series were produced simultaneously during the oxidation by nitric acid of a fatty material of high equivalent, it was reasonable to assume that each member of the dibasic series would be formed by a simple oxidation of the corresponding term of the monobasic series.[46] In order to test his hypothesis Dessaignes selected butyric acid as representative the monobasic fatty acids; the purified acid was prepared from fermented flesh or potato flour. He heated a mixture of butyric acid and twice its volume of nitric acid of density 1.40 inside a retort provided with a very long neck and inclined inside a water bath in such a way that the condensate of butyric acid always fell back into the retort. Nitric acid was added from time to time to replace the amount decomposed. After heating for about 24 hours, the liquor was distilled until it left a crystalline residue, tarnished by a substance attracting the humidity of the air. Dessaignes separated this particular substance by pressing it against paper and then subjected it to several tests. He promptly recognized that the crystals presented all the physical properties and chemical reactions of succinic acid. He ended his paper indicating that he did not have enough material to justify his conclusion by elementary analysis of the acid.[46]

Valeric acid

It was known that valeric (pentanoic) acid was little altered by the action of nitric acid; nevertheless, Dessaignes decided to study if a very prolonged reaction of these two acids also produced the same result. For this purpose he heated almost to boiling, and during 18 days, a mixture of nitric acid and valeric acid in the same apparatus he had used to study the conversion butyric acid into succinic acid.[19,48]. His results indicted that the products of this reaction varied in successive operations. When using valeric acid produced from valerian (*Valeriana officinalis*), the new acid formed was accompanied by another deliquescent acid, as well as by a neutral crystalline matter, containing nitrogen and possessing a slight odor of camphor. With valeric acid from potato oil, the accompanying material was a neutral nitrogenous oil, smelling like camphor.[48]

The mixture contained in the retort was distilled; the first half of the condensed liquid contained a colorless acid oil, which became solid or liquid according to the origin of the valeric acid employed. On pursuing the distillation, the retort was again filled with abundant red vapors; the operation was then stopped, and the residue of the retort was gently heated in a capsule until it has acquired a syrupy consistence. After some time, this syrup deposited thin crystals, which were easily purified by one or two crystallizations. The resulting acid was very pure, crystallizing in superb rhombohedral tables, which begun to sublime at 100 °C; it dissolved very well in warm water, and much less in cold water. From its physical and chemical properties, Dessaignes assumed that it was nitroangelic acid (2-methyl-2-butenoic acid), containing 41.37 % carbon, 4.82 % hydrogen, and 9.65 % nitrogen, corresponding to the formula $C_{10}H_4N_2O_8$.[48]

Boletic and fungic acids

Braconnot, during his extensive research on the composition of a variety of champignons, detected the presence of two new vegetable acids, which he named boletic acid and fungic acid.[49] Braconnot isolated these acids from *Boletus pseudo-igniarius* by expressing the juice from the mushroom, evaporating it to a sirupy consistency, followed by extraction with alcohol. The residue was then washed with alcohol, followed by solution in water and precipitation with silver nitrate. The precipitate was decomposed with hydrogen sulfide, the remaining solution evaporated, and the boletic and fungic acid isolated from the solid phase, and the mother liquid respectively.

Afterwards, in a similar work, Pompeious Alexander Bolley (1812-1870) proved that boletic acid was actually fumaric acid.[50]

In 1853, Dessaignes reported the results of his analyses of both acids. He extracted the boletic acid from the same mushroom where Braconnot had discovered it (*Boletus pseudo-igniarius*), and indicated that he also found it in small quantity in the fungi fly ascaric (*Amanita muscaria*) and deadly agaric (*Ammanita virosa*).[51] Boletic acid was very easily purified, owing to its sparing solubility in water. Dessaignes determined the composition of boletic acid and fumaric acid by combustion and from the analysis of their silver salts, and his results left no doubt as to the perfect identity of these two acids. He then went on to determine the composition of fungic acid. The residue left after removal of boletic acid was neutralized with ammonia and then precipitated with calcium chloride, in order to eliminate most of the calcium phosphate that was present. When the filtered liquor was heated, it suddenly deposited a white crystalline powder that after purification yielded concentrically grouped prisms, which, after some days, changed into large isolated crystals. These crystals burned without residue. All their chemical properties completely agreed with those of calcium citrate. The liquid from which the calcium citrate of lime had been precipitated was treated with lead acetate, and then with lead sub-acetate of lead, in order to extract the fungic acid. Dessaignes separated the acid as its ammonium salt, which was easy to purify by crystallization. This resulting acid presented all the characters of malic acid: when heated for a long time it was converted into fumaric acid and when almost entirely neutralized with lime, and heated to ebullition, it deposited a pulverulent salt of calcium, which, dissolved in weak nitric acid, gave crystals like those of calcium dimalate. Analysis of its silver salt gave 13.59 % carbon, 1.58 % hydrogen, and 62.13 % silver; corresponding very closely to that of silver malate 13.79 % carbon, 1.15 % hydrogen, and 62.57% silver. Fungic acid appeared to Dessaignes, therefore, to be only malic acid mixed with citric and phosphoric acids[50] (the same opinion stated by Bolley).[51]

Tartaric acids

Dessaignes carried on extensive research on the preparation, properties, and reactions of tartaric acids, and their derivatives.[7-12,15]

In his first paper he announced the discovery of two new acids resulting from the reactions of nitrotartaric acid. Finely divided tartaric acid was first dissolved in 4.5 times its weight of concentrated nitric acid and then mixed with an equal volume of strong sulfuric acid. After a day or so, most of the sulfuric acid was removed by pressing the mixture between two porous plates. The resulting white light mass, which released abundant white vapors when in contact with air; was purified by dissolving it in tepid water and then cooling the solution to 0 °C. Pressing it between two sheets of filter paper purified the ensuing crystalline mass. Dessaignes believed that the product he had prepared was nitrotartaric acid (he probably had a mixture with dinitrotartric acid). He now saturated the acid with ammonia and then added ammonium sulfide; on heating, the nitrate decomposed with abundant separation of sulfur. The filtrated solution was evaporated and left to crystallize as neutral ammonium tartrate. The aqueous solution of nitrotartaric acid, left alone or treated with a stream of hydrogen sulfide, or reacted with KOH or lead oxide, gave place to a series of compounds, among them, an acid having completely different properties from the ones described above. The aqueous solution of this acid, left alone at a temperature slightly above 0 °C, began to release bubbles of a gas mixture containing nitrogen oxide and CO_2, while changing its color to light blue. After the bubbling had ceased the solution was heated to about 40° to 50 °C and a new effervescence took place, now of pure CO_2. The solution was found to contain only oxalic acid. If the solution was heated only to 30 °C, the liquor began to release gas and to deposit a weight of acid inferior to that of the tartaric acid employed originally. This solid was found to contain very little oxalic acid.[7] According to Dessaignes, the acid appeared as voluminous prisms, melting at about 175 °C. Distilled rapidly, it produced another crystalline acid; very soluble, and slightly volatile. An aqueous reaction of the acid did not react with the chlorides of barium and calcium, the sulfates of magnesium and copper, ferric chloride, or ammonia. It precipitated the nitrates of lead and silver, mercurous nitrate, and mercuric chloride. An elemental analysis indicated its composition corresponded to that of an analog of malic acid. Dessaignes assumed that to satisfy this analogy the new acid had to be dibasic. He ended his paper stating that it would of interest to study the behavior of these two acids under polarized light.[7]

In a following paper Dessaignes mentioned that he had decided to name tartronic acid the new acid produced by the spontaneous decomposition of an aqueous solution of nitrotartaric acid. This acid, heated in a retort to 160 °C, released a large amount of CO_2 and a particular acid odor. Increasing the temperature to 180 °C and maintaining it at that level until the gas release had ceased, left in the vessel a colored viscous matter, which on cooling solidified into a fragile mass. Upon washing with warm water and drying, it turned into a white insipid powder, insoluble in cold water, slightly soluble in hot water, and melting at about 180 °C. Dessaignes dissolved it into enough hot aqueous KOH to neutralize it and found that it was not precipitated by metallic salts, except silver nitrate. The resulting precipitate crystallized spontaneously and was soluble in hot water. Separation of the acid by means of HCl, and elemental analysis gave a composition corresponding to the glycolic acid (hydroxyacetic acid) extracted from gelatin sugar. Dessaignes believed that the insoluble residue remaining in the retort probably was to glycolic acid what lactide was to lactic acid.[8]

In the following publication, Dessaignes remarked that the formulas of succinic, malic, and aspartic acids born the same relation that existed between the formulas of acetic acid, hydroxyacetic acid, and glycocoll (glycine). Tartaric acid seemed to form part of the first family of acids, and if malic acid was oxysuccinic acid, then it was possible to consider tartaric acid to be dioxysuccinic acid. He also wrote that although it was probably very difficult to superoxidize succinic acid, he had succeeded in reducing tartaric acid and transforming it into succinic acid. To do so, he treated powdered tartaric acid with phosphorus iodide in a sealed tube and heated for several days. The tube was then broken and the contents diluted with a little amount of water; evaporation of the water led to the formation of crystals which Dessaignes identify with succinic acid.[10]

In a continuing publication, Dessaignes proved that if was possible to convert tartaric acid into malic acid by deoxidation. To do so, he used the fact that he had found malic acid in the mother liquor obtained when tartaric acid was converted into succinic acid by means of phosphorus iodide. The phosphoric acid was eliminated by cooling the mother liquor and saturating it with limewater. The solution was filtrated, then precipitated with lead acetate, and the precipitate decomposed with hydrogen sulfide. Further treatment allowed separating the new material into succinic acid, tartar cream, and pure malic acid.[11]

In another publication, Dessaignes reported that the production of tartaric acid by oxidation of lactose, and of dulcin by oxidation of the racemic acid, had suggested him the possibility of obtaining *levo*-tartaric acid directly by treating with nitric acid sorbose, which was known to deviate to the left polarized light. By following a procedure suggested by Liebig for the two oxidation processes mentioned above,[52] he was able to isolate two acids, one the ordinary racemic one (characterized by the shape and composition of its calcium salt), and the other, dextro-tartaric acid.[12]

By treating acid syrup first with calcium acetate and then with lead acetate, he observed the appearance of two new acids, which he named aposorbic (trihydroxypyrotartaric) acid and *meso*-tartaric acid. Aposorbic acid usually crystallized in plates, melting at about 100 °C while losing water: it boiled and becoming colored at 170 °C, and turning into a black bullous mass at 200 °C. Dessaignes described the silver, calcium, and lead salts of the acid, as well as its behavior with ammonia. Meso-tartaric acid crystallized in rectangular plates; was very soluble in water, and on heating lost water slowly, which it recovered when put in contact with air. Analysis of the hydrated acid indicated that it had the same composition as racemic acid. Dessaignes also described the silver, calcium, and lead salts of the acid.[12]

Amides

In a paper published in 1852, Dessaignes described a series of new combinations obtained from natural and synthetic amides, particularly with mercuric oxides. He showed that even the most neutral of these amides combined easily with the oxide prepared by the wet via. The reaction took place without elimination of water or with the elimination of one equivalent of water. The amides studied were urea, oxamide, fumaramide, butyramide, benzamide, glycine, and asparagine. Dessaignes gave a detailed preparation procedure of the amides, their properties, and elemental formula.[22]

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