Edme Alfred Bourgoin

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RESUMEN. Edme Alfred Bourgoin (1836-1897), un farmacéutico, médico y político Francés, estudió la composición química del cerebro, determinó la naturaleza del principio activo de la senna y del boldo, la electrólisis de numerosos ácidos y sales orgánicas, el papel del agua en la electrólisis, la solubilidad de ácidos orgánicos en agua y otros solventes, y describió la preparación y propiedades de una serie de nuevos compuestos bromados. En la parte final de su vida se opuso intensamente contra las ideas de Louis Pasteur y a la enseñanza de experiencias prácticas de laboratorio en la educación universitaria.

ABSTRACT. Edme Alfred Bourgoin (1836-1897), a French pharmacist, physician, and politician, studied the chemical composition of brain, the nature of the active principle of senna and boldo, the electrolysis of many acids and organic salts, the role of water in electrolysis, the solubility of organic acids in water and other solvents, and described the preparation and properties of many new bromine derivatives. In the last part of his life, he actively opposed Louis Pasteur’s ideas and the teaching of practical laboratory experiences.

Life and career

No information seems to be available about the early life and education of Edme Alphonse Bourgoin. He was born on May 27 1836 at Saint-Cyr les Colons (Yonne), France, where his father worked as operator of a Chappe telegraph.

In 1858 Bourgoin was awarded a pharmacy internship at the pharmacy of the hospitals of Paris, and from there on he went through a series of important appointments, elections, and awards: Laureate of the hospitals (1860), pharmacist of the Midi hospital (1862), degree of physical sciences (1862), degree of medical doctor (1863)2, chief pharmacist of the children’s hospital (1867-1884), Laureate of the Société de Pharmacie (1868), member of the Société de Pharmacie, member of the council of the Société Chimique de Paris, member of the Société de Pharmacie of Indre, member of the Société Royale de Pharmacie of Bruxelles, professor of medical pharmacy at the l’École Supérieure de Pharmacie (1877), member of the Société de Médecine de Paris (pharmacie section) (1879), member of the Conseil d’Hypothèse Publique (1880), chief pharmacist and director of the central pharmacy of the Parisian hospitals (1884), officer of the Légion d’honneur (July 9, 1891), and twice Laureate of the Institut de France (Jecker and Berbier prizes). In 1893 he was elected member (deputy) of the Legislative Assembly, as representative of the constituency of Vouziers. While in the latter position, he died suddenly of a brain hemorrhage (February 10, 1897). Two days later he was buried in the Montmartre cemetery.

Between 1867 and 1868 Bourgoin carried on extensive research on the electrolysis of organic acids and their salts, at the laboratories of Marcellin Berthelot (1827 - 1907) in the École de Pharmacie. As a result of this work he was awarded his diploma of pharmacist of first class by the École de Pharmacie (1867)4, passed successfully the competitive examination of the École to begin an academic career (1869)3, and the Université de Paris awarded him a doctoral degree in physical sciences (1868)8.

The last years of his life were characterized by a strong opposition to the ideas of Louis Pasteur (1822-1895) and to the introduction of practical laboratories in the teaching of high education.1
SCIENTIFIC CONTRIBUTION

Bourgoin published about 80 papers and books in his different areas of interest: brain chemistry, electrochemistry, solubility of organic acids, bromine derivatives, organic chemistry, and natural principles. He was one of the main contributors to the Encyclopédie Chimique, published by Edmond Frémy (1814-1894).

Composition of the brain

Although many scientists had examined the chemical composition of the brain, there were still many unanswered questions. In his first scientific publication, Bourgoin provided additional qualitative and quantitative experimental results and proved that cerebrin did not contain phosphorus, contrary to the opinion of most authors. The first set of experiments was devoted to determining the amount of water present in the brain. The reported figures varied between 75 to 88%; according to Bourgoin the difference stemmed from the fact that brain was the most hygroscopic tissue of the body. For this reason, in the determination of the water content it was necessary to take a series of precautions, for example, not to use wet clothes, to carry the analysis as soon as possible, etc. It was also of interest to determine the relative amounts of white and gray substances. A weighed number of thin layers of human brain were put to dry in a stove heated previously to 75°C and towards the end the temperature was raised to 90°C, to achieve total dryness (at 100°C the brain substance experimented a clear alteration). The average result of seven experiences indicated that the white (obtained from the anterior lobes) and the gray substances (obtained from the circulations) contained 73.5 and 83% water, respectively. The overall brain substance contained 79% water.

The phosphorus content was determined by mixing a given quantity of dried brain with 20 times its weight of a mixture of sodium carbonate and potassium nitrate, and pouring the mixture in small portions into a platinum crucible heated dark red. The residue was first treated with distilled water saturated with HCl, then neutralized with ammonia, followed by addition of a solution of magnesium sulfate. After filtration, the solution was calcined in a platinum crucible; the dry weight multiplied by 0.2793 gave the quantity of phosphorus present. The results of six experiences indicated that the phosphorus content varied in a wide range, that the gray substance contained a larger percentage of phosphorus than the white one, and that the central part contained about 2% phosphorus (dry basis). J. P. Couerbe (1805-1867) believed that the variation in phosphorus content was related to the intelligence of the individual. Bourgoin thought that other explanations were also possible; one of his brain samples belonged to an emaciated man who had died of tuberculosis of the third degree, its brain weight was very low but contained the highest percentage of phosphorus. Did these facts indicate that the brain, preferable to other principles absorbed, fatty materials exempt of phosphorus? It was very possible that in cases of emaciation the brain behaved as other body tissues. Analysis of the nitrogen content in the brain showed that it also varied in a wide range and that the gray matter contained much more this element than the white one.

The next step was determination of the overall composition of the brain. Extraction with boiling alcohol left a residue, which was found to be composed of albuminous substances. To determine if these substances were present in the brain in a soluble and insoluble state, Bourgoin took a quantity of fresh brain mashed to a pulp and extracted it first with cold distilled water and then brought the solution to boiling. From the weight of the dried coagulum he concluded that about 25% of the albuminoidal substance contained in the brain were in a soluble state. The original alcoholic extract was found to contain cerebrin, cholesterol, and fatty materials. The result of these analyses indicated that human brain contained 80% water, 1.70% cerebrin, 7.80% cholesterol and fatty materials, 2.28% soluble albuminous matter, 6.82% insoluble albuminous matter, and 1.40% of aqueous nitrogenous extract. The aqueous extract was acid and extremely hygroscopic, it contained a small amount of free phosphoric acid and about 8.03% of nitrogen.

The last experiments were devoted to determine the composition of cerebrin. This material was obtained impure by drying thin layers of brain at temperatures between 75°C and 80°C, powdering the dry residue, extracting it with concentrated boiling alcohol, and cooling the resulting extract. The precipitate formed was found to contain cerebrin, cholesterol, fatty materials, and oleophosphoric acid, and was partially purified by washing with cold alcohol, followed by several extractions with ether. It was further purified by several extractions with warming alcohol. The resulting cerebrin appeared as bright white grains, insoluble in cold water and swelling in contact with hot water. It was insoluble in cold and hot ether, very soluble in boiling alcohol and in chloroform. Chemical analysis indicated that it contained between 66.35% carbon, 10.96% hydrogen, 20.38% oxygen, 2.29% nitrogen, and no phosphorus. This composition corresponded approximately to the global formula $C_{27}H_{21}O_{16}$, fitting that of an amide of dioixioleic acid. Bourgoin remarked that this analysis and formula were very approximate because it was hard to determine that his sample was strictly pure.

In 1874 Nicolas Théodore Gobley (1811-1876) published a paper reporting that he had found that cerebrin was present in egg yolk, closely united with lecithin. He had isolated cerebrin by treating with ether the fatty material separated by means of an alcoholic extraction. The insoluble part was mainly composed of cerebrin, which could be purified by successive extractions with boiling alcohol. Gobley reported that cerebrin was a colorless inodorous solid, which when dry melted between 155°C and 160°C. Heated below this temperature it turned brown and...
decomposed. It was slightly soluble in ether and not colored blue by HCl. Chemical analysis indicated that it contained 66.85% carbon, 10.82% hydrogen, 20.04% oxygen and 2.29% nitrogen.

In a critical note, Bourgoin indicated that his procedure for separating cerebrin from brain tissue was substantially simpler that of Gobley, and showed that his analytical results were essentially the same as those of Gobley.16

Natural products

Senna

Senna (Senna Alexandrina) had been analyzed by many scientists, among them Edmée Bouillon Lagrange (1764-1844)17, Jean-Louis Lassaigne (1800-1859) and H. Feneulle18, and Melchior Kubly and Johann Georg Dragendorff (1836-1898)19.

Bouillon-Lagrange prepared an infusion and a tisane of senna and treated it with a number of reagents and reported the properties of the different fractions obtained. The solution operated as a purgative only in the presence of oxygen; in the absence of this element it had no medicinal action. The limited techniques available to Bouillon-Lagrange did not allow him to separate the active principle present in the plant.17 This was the reason that led Lassaigne and Feneulle, to extend Bouillon-Lagrange’s work. After a comprehensive set of experiments they concluded that the leaves of senna contained chlorophyll, fatty oil, volatile oil, albumen, an emetic principle, which they named cathartin, a yellow coloring material, malic acid, calcium malate and tartrate, potassium acetate, and other mineral salts. They reported that cathartin was a non-crystallizable and deliquescent material, having a yellow red color, a particular smell, and a bitter and nauseous taste. It was completely soluble in water and alcohol and insoluble in ether. Its aqueous solution precipitated the gallnut infusion and was not precipitated by iodine, lead acetate, KOH, NaOH, and ammonia.18 Some years later Kubly and Dragendorff reported that senna owed its properties to a particular acid, which they named cathartic acid; but they did not provide sufficient information to prove their claims.9,20

The contradictory information available in the literature led Bourgoin and E. Bouchut to carry additional experiments to try to identify the nature of the substance(s) responsible for the purgative properties of senna.21 To do so they treated one kilo of Alexandrian senna with ten times its weight of boiling distilled water. The mixture was expressed and filtered and the resulting liquor concentrated to two liters by evaporation in a water bath. Addition of an equal volume of alcohol caused the precipitation of an abundant mucilaginous matter that was separated. The filtered liquid was concentrated by evaporation and used to prepare the assumed cathartin of Lassaigne and Feneulle and cathartic acid of Dragendorff and Kubly. Bourgoin and Bouchut reported that analysis of the different phases they separated in their procedure.

The mucilaginous matter was dissolved in distilled water; the resulting non-bitter solution was administered to a group of 15 children of different ages and found to have no purgative effects (the same group of children was used for the tests described below). The alcoholic extract was evaporated in a water bath to eliminate most of the solvent; the resulting dark brown concentrate was bitter, slightly nauseous, did not precipitate with water or ordinary alcohol, yielded an abundant precipitate with absolute alcohol, and had a strong purgative effect on the children.21

To prepare cathartin, Bourgoin and Bouchut used a simpler procedure than the one reported by Lassaigne and Feneulle. Senna was digested with distilled water and the resulting solution heated to boiling and then left to cool. After twenty-four hours it was pressed, filtered, treated with alcohol to separate the mucilaginous matter, evaporated in a water-bath to eliminate most of the solvent, and then treated with lead acetate. The resulting abundant precipitate was rejected and the liquid treated with hydrogen sulfide to eliminate the excess of lead acetate. The resulting liquid was evaporated to a syrupy consistence, treated with rectified alcohol, filtered, mixed with very dilute sulfuric acid; filtered again, and evaporated in a water bath. The resulting reddish-yellow substance had a bitter nauseous taste, recalling that of senna, was hygroscopic, soluble in water and in alcohol, but not completely in ether. An aqueous solution gave an abundant precipitate with lead sub-acetate, became darker under the influence of alkalai, and found to have slight purgative effect on the children. Since senna was known to contain only 1/30ths of its weight in cathartin, it was clear that this preparation evidently had not the strength of the liquid extract, and consequently could not represent by itself the purgative principle of senna.21

Bourgoin and Bouchut found that the concentrated water infusion obtained after separation of the mucilaginous substance, contained a new material, which had not been reported previously. This substance, which was very soluble in water and insoluble in concentrated alcohol and in ether, was isolated by successively treating the filtered liquid with lead acetate, hydrogen sulfide, and concentrated alcohol. A 10% aqueous solution of the residue was found to have no effect on the children.21

Cathartic acid was obtained by mixing a concentrated infusion of senna with its volume of 75% alcohol, to precipitate most of the mucilaginous substance. The filtrated liquid was concentrated again and precipitated with absolute alcohol. The resulting black precipitate of cathartic acid was dissolved in water, precipitated by dilute HCl, and purified by successive treatments with absolute alcohol, a weak solution of KOH, and HCl. One kilogram of senna yielded six to seven grams of pure cathartic acid. Since cathartic acid was insoluble in water, it was neutralized with diluted KOH to obtain an aqueous solution containing 1% weight of the salt. Physiological tests with the
children group showed cathartic acid could not be considered to be responsible for the complete purgative action of senna.21

Bourgoin and Bouchut believed that the cathartin of Lassaigne and Feneulle was not a definite principle, but should be considered to be a mixture of many substances, of which one at least was purgative. In order to determine to which portion of the product the purgative properties could be attributed, they repeatedly mixed cathartin with dry ether, evaporated the ethereal extract in a water bath, and extracted it with concentrated alcohol. The residue was found to have all the properties of an acid, which Bourgoin and Bouchut named chrysophanic acid. The acid was sparingly soluble in water and very soluble in alcohol and ether. The ethereal solution was yellow, reddened litmus paper, and turned red on addition of alkalis. The resulting salts were very soluble in water, a fact that allowed separation of the organic acid by means of acetic acid. This product was made up into pills, each containing 10 centigrams. All these results indicated that the purgative principle contained in cathartin should be present in the portion insoluble in ether. Physiological tests corroborated this hypothesis: cathartin freed of all the substances soluble in ether, produced uneasiness, loss of appetite, nausea, some griping, and several evacuations.21

Some years later Bourgoin published another paper about the complex nature of cathartin where he repeated that he had found that this substance was actually a mixture of at least three different compounds, chrysophanic acid, a dextro glucoside, and chrysophanin. In this new paper he gave a detailed procedure for preparing each of these substances, and their properties

According to Bourgoin, cathartin was an acid substance, sparingly soluble in water, soluble in alcohol, ether, and alkalis, the solutions having a beautiful red color. The latter property could be used to show its presence in the leaves; it was enough to prepare an infusion and add a few drops of ammonia to observe the red coloration.22

Cathartin could be separated from chrysophanic means by means of ether extraction. Addition of beer yeast to the aqueous solution resulted in the appearance of alcohol and release of CO₂. The solution strongly reduced the FeH₂O reagent. Elimination of the chrysophanin present yielded a solution, which deviated polarized light to the right. All these properties were a clear proof of the presence of a dextro glucoside, easily separated by successive treatment with lead subacetate and hydrogen sulfide. Chrysophanin was obtained by extraction with ether, followed by treatment with lead subacetate, and regeneration of chrysophanin by decomposition of the lead compound with hydrogen sulfide.22

Bourgoin remarked that the results of his experiments clearly proved that the cathartin of Lassaigne and Feneulle was actually a mixture and that the term cathartin should be eliminated from the chemical lexicon.22

**Boldo**

In 1872 Bourgoin and his student Jean Claude Verne (1846-1925)23 reported that they had separated boldina, the active principle present in the leaves of boldo, a tree indigenous to Chile and belonging to the order Monimiaceae (the leaves of boldo have a strong piquant camphorate savor, and contain an essential oil and an organic alkali). Bourgoin and Verne indicated that boldo was the *Boledoa fragrans* of Antoine Laurent de Jussieu (1748-1836), the *Rutizia fragrans* of Hipólito Ruiz (1754-1816) and José Luis Pavón, the *Paemia fragrans* of Jules Persoz (1805-1888), and the *Peumus boldus* of H. Baillon (1827-1895).24

Bourgoin and Verne exhausted the powdered leaves of boldo with washed ether in a displacement apparatus and obtained a saturated aromatic tincture. Distillation of the tincture indicated that it was composed of several complex volatile products, distilling at 185⁰, 230⁰, and about 300⁰C. The residue of the ethereal extract was repeatedly exhausted with a solution of tartaric acid in 90⁰ alcohol and the alcoholic extract evaporated until it became acetic syrup. This syrup was treated with ether to remove a brown odorous matter, soluble in ether, alcohol, and acids. This matter was neutralized with potassium bicarbonate and then re-extracted with ether, to remove a substance presenting all the characteristic reactions of an alkaloid; this was impure *boldina*. Impure boldina was further purified by dissolution in water slightly acidulated with acetic acid, and then precipitated by ammonia added in slight excess. The results indicated the leaves contained about one part of alkali per one thousand parts of leaves.24

Bourgoin and Verne developed a large-scale process for preparing boldina: The leaves, coarsely powdered, were first extracted with water acidulated by 30 g of acetic acid per kilo of product, and the extract filtered and evaporated in a water-bath to the consistency of thick honey. The resulting acid residue contained, beside the alkaloid, a little aromatic matter and a large quantity of calcium acetate. Replacement of the acetic acid by citric or sulfuric acid yielded a solution, which mixed with alcohol, produced a voluminous precipitate of calcium citrate or calcium sulfate, respectively. Washing with ether, saturating with potassium bicarbonate, and extracting the alkaloid with ether, finished the operation. Upon evaporation a residue was left which was dissolved in diluted acetic acid and then precipitated by ammonia. It was usually necessary to repeat this process to rid the alkaloid of a small quantity of yellow matter.24

Bourgoin and Verne reported that boldina was sparingly soluble in water; the resulting solution was alkaline and had a perceptibly bitter taste. Boldina was soluble in alcohol, ether, chloroform, caustic alkalis, and benzene. From solution in acids it was precipitated by ammonia and the double iodide of mercury and potassium. Concentrated nitric acid or cold sulfuric acid immediately colored it red.24
**Adulteration of bitter almond**

Bitter almond essence was widely adulterated, particularly with nitrobenzene. Different methods have been indicated for the recognition of this adulteration, but none of them was really satisfactory. One of them was based on the fact that nitrobenzene was much denser than the essence; hence a measurement of the specific density of the suspected oil could suggest the presence of the nitro compound, but usually the offenders also added alcohol or other light liquid, to obscure the falsification. Dragendorff had suggested adding a few drops of alcohol to a small quantity of the essence, and introduce a globule of sodium; the coloration became deeper in proportion to the amount of nitro compound present. Marcellin Berthelot (1827-1907)\(^2\) had suggested distilling the mixture with iron filings and acetic acid, neutralizing the distillate by a trace of lime, and then seeking to produce a violet coloration by the addition of a diluted solution of calcium hypochlorite. This process was extremely sensitive when tested on pure nitrobenzene, for a single drop could be recognized by this method. Unfortunately, the presence of bitter almond oil affected the reaction in an unknown manner, a negative result being often obtained with mixtures, which contained as much as 40% of nitrobenzene.\(^2\)

Bourgoin proposed a simple alternative method for detecting this adulteration: One part of the essential oil was agitated in a test-tube with about half its weight of pure caustic potash. If the essence was pure, it assumed only a yellowish coloration; but if it contained nitrobenzene, the yellow color rapidly changed to a reddish yellow, which disappeared in less than a minute, giving place to a green coloration. Upon addition of a small quantity of water split the mixture neatly into two phases, a lower yellow layer, and an upper green one, which became red in a few hours. The presence of alcohol did not affect these reactions, actually it seemed to favor them, for the mixture became hot, and the green color was rapidly developed.\(^2\)

In a following note, Bourgoin remarked that since his procedure was only qualitative he had developed another one to make the analysis quantitative.\(^2\)\(^3\) His method consisted in mixing under agitation 5 to 10 g of the essence with 20 to 40 cm\(^3\) of a concentrated solution of sodium bisulphite, followed by addition of washed ether to extract the nitrobenzene. The ethereal phase was separated, filtered through paper, and then evaporated in a water bath. The weight of the residue indicated, quite well, the amount of foreign material present in the essence. To insure that the residue was nitrobenzene, it was mixed with acetic acid and a small amount of iron filings. The distilled product was neutralized with calcium hypochlorite: formation of a violet blue color indicated the presence of aniline.\(^2\)\(^7\)

**Electrolysis of organic acids**

In his first publication on the subject, Bourgoin exposed his general ideas about the theory of electrolysis. He wrote that the current theories claimed that the action of an electric current on organic salts was quite different from that it exerted on mineral salts, because it liberated a wide variety of compounds, such as radicals, which split at the time of their formation, aldehydes, hydrocarbons, etc.\(^2\)\(^8\) Nevertheless, Bourgoin held a different opinion, he believed that the action of an electrical current on acids and their salts was universal, independent of the organic or inorganic nature of the compound. The basic element separated at the positive pole while the elements of the anhydrous acid and oxygen, which matched the basic hydrogen or metal, separated at the negative pole. If this universal law did not seem to appear in a general manner, it was then necessary to look for the cause in the nature itself of organic acids. As an example, Bourgoin mentioned that in the case of a mineral salt, such as potassium sulfate, no oxidation was possible at the positive pole. As a consequence, oxygen, which represented the basic element, was liberated there. In the case of an organic salt, the reaction was the same, except that in the positive pole the nascent oxygen could induce oxidation phenomena and react with the carbon, with the hydrogen of the acid, or with both elements simultaneously. Oxygen reacted preferentially with carbon, in a ratio determined by the composition of the acids and its metal; hence Bourgoin named the reaction the *characteristic reaction of an organic acid*. Thus, acetic acid yielded 2 moles of CO\(_2\) and one mole of ethane, succinic acid 2 moles of CO\(_2\) and one mole of ethylene, and tartaric acid 2 moles of CO\(_2\) and one mole of acetic acid. When an organic salt was electrolyzed in the presence of an excess of alkali, the latter behaved like a salt, liberating oxygen at the positive pole; there the oxidation of the elements of the acid could be stronger than the normal case where the acid alone was decomposed. In this situation succinic acid would convert completely into CO\(_2\) and water.\(^2\)\(^8\)

Bourgoin summarized his understanding as follows: (a) The electrolysis of mineral and organic salts resulted in the liberation of a metal or basic hydrogen at the positive pole and the elements of the anhydrous acid or oxygen of the acid or salt at the negative pole; (b) the electrolysis of organic acids and salts resulted in (i) the normal oxidation of the acid or salt by the oxidation, yielding a metal or basic hydrogen at the positive pole, and the elements of the anhydrous acid or the oxygen of the acid or salt, accompanied by CO\(_2\), hydrocarbon, aldehyde, acid, etc., at the negative pole, or (ii) acid and oxygen of the acid or the salt, and oxygen of the water, accompanied by secondary oxidation products, at the negative pole.\(^2\)\(^8\)

In a following paper, Bourgoin wrote that he intended to use the results of his work on the electrolysis of acetic acid, as a first example for the justification of his theory.\(^2\)\(^9\) His experimental apparatus consisted of a tube having at its bottom a small perforation of 0.4 mm diameter and closed at the top with a natural rubber cap. Through the cap passed an almost capillary syphon tube, as well as a platinum wire, which terminated inside the tube in a platinum
plate of metal and formed one the electrodes. This tube was encircled by a larger one of such capacity that when the
disengaged gas in the interior exerted a pressure of 4 cm Hg, the volume of solution in each tube was be the same. The
second electrode was located in the annular space formed by these tubes. This arrangement permitted collecting at
will the gas released at the electrodes and sampling the liquid without stopping the current. The current passed from
one pole to the other through the small orifice at the bottom of the internal tube [for a detailed drawing of the
apparatus see reference 4]. Experiments were made with (1) a neutral concentrated solution of potassium acetate to
determine the true action of the current upon acetate, (2) a solution of mixture of acetate and alkali, and (3) a solution
of pure acetic acid.

Bourgoin results indicated that (a) the current acted on potassium acetate of potassium as on a mineral substance;
(b) in a moderately alkaline solution the oxygen reacted on the elements of the anhydrous acid, producing a normal
oxidation, with the resulting release of CO₂ and ethane; (c) a certain quantity of the acid was totally consumed under
the influence of oxygen furnished either by the salt or by the alkaline water; (d) the two poles suffered unequal losses
of the salt; almost the whole of the salt, which disappeared, occurred at the positive pole; (e) the current acted on the
free acetic acid in the same manner as in sulfuric acid, concentrating it at the positive pole; (f) the gas evolved during
the electrolysis was chiefly composed of oxygen, with some CO₂ and a little CO; (g) an equimolar solution of
potassium acetate and an alkali, evolved at the positive pole only oxygen.²⁹

The following work was related to the electrolysis of tartaric acid under the same conditions as the electrolysis of
acetic acid.³⁰ During the electrolysis of a concentrated solution of pure neutral potassium tartrate the liquor became
alkaline at the negative pole; a moderate amount of gas was released at both poles, the solution of the positive pole
remained neutral, accompanied by a slow and continuous precipitation of potassium bitartrate (cream of tartar), and
the gas evolved at the positive pole was composed of CO₂, oxygen, CO, and nitrogen. Most of the salt decomposition
occurred at the positive pole.

The action of the current on a mixture of neutral tartrate and alkali produced quite different results to those
obtained with neutral tartrate only, notwithstanding that the fundamental action was the same. A mixture of CO₂, CO,
oxxygen, CO₂ and ethane was released at the positive pole The decomposition of free tartaric acid yielded the same
products as the neutral tartrate, though in different proportions, while acetic acid was formed at the positive pole.³⁰

Pyrotaurinic acid was found to be very stable under the influence of an electrical current. A cold, almost saturated
solution released a very small amount of gas, even when the electrodes were positioned very close one to the other.
Hydrogen was generated at the negative pole and oxygen at the positive one; the latter gas containing very small
amounts of CO₂ and CO. The acid became concentrated in the positive compartment of the cell. All these results
indicated that pyrotaurinic acid electrolyzed like mineral acids.³¹

Other acids studied using the same apparatus and experimental technique included formic,³² benzoic,³³ oxalic,³⁴
succinic,³⁵ malic,³⁶ and phthalic acids.³⁷ Bourgoin also studied the electrolysis of the sulfates of atropine, brucine, and
codeine,³⁸ of mixtures of formic and acetic acids, formic and benzoic, acetic and benzoic acids, of ammonium sulfate,
sulfuric acid, nitric acid, boric acid, camphoric acid, malonic acid, etc. etc.⁴,⁶,³⁷,⁴¹

For example, the electrolysis of a neutral solution of benzoic acid yielded KOH at the negative pole and benzoic
anhydride and oxygen at the positive one; the same reaction took place with a solution containing a slight excess of
KOH, except that acetylene was also released. A very strong reaction took place with a very alkaline solution, the
solution remained colorless after 48 hours. After 24 hours the gas released contained CO₂, CO and acetylene.
Bourgoin reported that a cold solution of benzoic acid was hardly electrolyzed, even when the electrodes were located
very closely. The gas released was pure oxygen.³³

An aqueous solution of phthalic acid was found to be a poor conductor of the current. At the end of two days only
36.5 cm³ of gas were collected at the positive pole of a battery composed of ten Bunsen elements; this gas proved to
be pure oxygen and originated completely from the acid. Analysis of the liquid in each compartment showed that a
concentration of the solution had taken place at the positive pole, and that the quantity of acid electrolyzed corresponded to the oxygen evolved. According to Bourgoin, these results showed that the current had not
decomposed the water, but the acid reacted according to C₇H₆O₄ = (C₇H₆O₃+ O) + H₂ at the negative pole, and
(C₇H₆O₃ + O) + H₂O = C₇H₆O₃+ O₂ at the positive one [Bourgoin repeated in several publications his claim that water
was not an electrolyte and that in electrolysis it only played the role of a solvent or hydrating agent⁴]. A concentrated
solution of neutral potassium phthalate was readily electrolyzed. Hydrogen only was released at the negative pole
while the liquid in the corresponding compartment became strongly alkaline. At the positive pole the gas released
contained oxygen mixed with appreciable quantities of CO₂ and CO, and a crystalline layer of pure phthalic acid was
deposited on the electrode.³⁷

Since it was known that in chemical reactions boric acid behaved as an acid or as a base, Bourgoin decided to
investigate if this dual behavior also took place under the influence of a current. Electrolysis of a saturated cold
solution of borax in a cell composed of four elements showed that oxygen and hydrogen were released at the poles
and that the solution had become strongly alkaline at the negative pole and acid at the positive one. All the alkali was
electrolyzed, while part of the acid accumulated at the positive pole. These facts proved that that under the influence
of an electric current, borate behaved as a true acid. Nevertheless, an electrical current did not affect an aqueous solution of pure boric acid. Bourgoin used part of the above experiments to prove that the gas generated during the electrolysis of a mixture of potassium acetate (and potassium formiate), was not dimethyl (methyl methyure, derivative of the methyl radical), as claimed by Hermann Kolbe (1818-1884) but ethane.

The role of water in electrolysis

Bourgoin devoted a particular memoir for discussing the role played in water during electrolysis. His basic argument was that water was not decomposed in an electrolytic process; it only behaved as a solvent or as a hydrating agent. Addition of acid or alkali produced electrolysis but the acid or the alkali were the subjects of the action of the current. To prove his contention, he described in quantitative detail the results of the electrolysis of aqueous solutions of KOH, sulfuric acid, boric acid, and organic acids, using the experimental apparatus described above.

For example, the electrolysis of a highly diluted solution of KOH showed that the alkali was concentrated at the negative pole and oxygen released at the negative one. The latter originated from the electrolyzed alkali, according to \( \text{KOH} = \text{KH} (+ \text{pole}) + \text{O} (- \text{pole}) \). At the negative pole the hydrogen of the residue decomposed and the metal generated reacted with water, regenerating the alkali and releasing hydrogen: \( \text{K} + \text{H}_2\text{O} = \text{KOH} + \text{H} \). The latter reaction explained the accumulation of alkali at the negative pole. If these were the equations taking place, then the amount of gas collected at the negative pole should be twice larger than that corresponding to the electrolyzed alkali. According to Bourgoin, the numerical result of his experiments proved this assumption to be true: 0.00665 atoms of hydrogen were collected for 0.187 moles of KH, containing 0.0065 atom of hydrogen. In other words, although the oxygen produced originated exclusively from KOH, the hydrogen originated from two sources, one KOH itself, and the other, a secondary reaction due to the presence of an alkaline metal. Bourgoin returned to his claim in a later publication.

Solubility of organic acids

Bourgoin measured the solubility of a series of organic acids in water and other solvents. The first work related to the solubility of succinic acid in water. In his opening statements Bourgoin showed that the data reported by several author were widely different, probably because the acid used was not sufficiently pure. For this reason, his first efforts were devoted to prepare succinic acid as pure as possible by successive crystallizations. The solubility of the acid in distilled water up to 50°C was determined by first heating the solution and then letting it cool until the desired temperature was reached. The solution was then strongly agitated with an excess of succinic acid, to avoid supersaturation. The filtered liquid was then titrated with baryta water. Bourgoin reported the solubility at 7 temperatures levels within 0° and 48°C. For values above 50°C (78° and 100°C) he used a gravimetric method, in which the water was evaporated and the dry residue weighed. The results indicated that the solubility increased rapidly with temperature above 50°C.

In a following work, Bourgoin used the same experimental technique to measure the solubility of benzoic and salicylic acids in water, at twelve temperatures between 0° and 75°C. These acids were known to be very soluble in alcohol and ether and sparingly soluble in water, particularly cold water. The results indicated that the solubility curves crossed at about 40°C; below this temperature benzoic acid was slightly more soluble than benzoic acid, and the above it slightly les soluble. At 0°C and 75°C the solubility values were (1.50; 25.50) and (1.70; 22.0) g/L, respectively.

A third memoir reported the solubility of oxalic, succinic, tartaric, citric, gallic, benzoic, salicylic, and phthalic acids in alcohol (of 90°, and absolute) and ether at 15°C, using the same technique as before. The results were as follows (g/L): (Table 1)

<table>
<thead>
<tr>
<th>Acid</th>
<th>Ether</th>
<th>Alcohol Absolute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic</td>
<td>1.266</td>
<td>23.73 14.70</td>
</tr>
<tr>
<td>Succinic</td>
<td>1.265</td>
<td>7.51   12.59</td>
</tr>
<tr>
<td>Tartaric</td>
<td>0.400</td>
<td>25.604 41.135</td>
</tr>
<tr>
<td>Citric</td>
<td>2.26</td>
<td>75.90 52.85</td>
</tr>
<tr>
<td>Gallic</td>
<td>2.56</td>
<td>38.79 23.31</td>
</tr>
<tr>
<td>Benzoic</td>
<td>31.35</td>
<td>46.68 41.62</td>
</tr>
<tr>
<td>Salicylic</td>
<td>50.47</td>
<td>49.63 42.09</td>
</tr>
<tr>
<td>Phthalic</td>
<td>0.684</td>
<td>10.08 11.70</td>
</tr>
</tbody>
</table>
Bromine derivatives
Bourgoin published a large number of short communications describing the preparation and properties of a series of bromine derivatives. Some of them were the following:

Preparation of oxymaleic acid
This acid was prepared by the action of freshly prepared silver oxide on a cold solution of barium monobromomaleate. The bromate separated as silver bromide and the resulting solution of potassium oxymaleate was filtered, precipitated with lead acetate, and the lead oxymaleate decomposed by hydrogen sulfide. On evaporating the solution and crystallizing the product from ether, the oxymaleic acid was obtained as long, slender crystals, very soluble in water, alcohol, and ether. The alkaline salts of this dibasic acid were crystalline and very soluble in water; the silver oxymaleate was found to be unstable, it decomposed when heated with water and exploded when heated in dry state. According to Bourgoin, oxymaleic acid (C₂H₄O₅) differed from maleic acid (C₄H₄O₄) by two equivalents of oxygen and from malic acid (C₄H₆O₄), by two equivalents of hydrogen.⁴⁹

Pentabromoethane
Bourgoin prepared this compound by heating a mixture of 30 g of perbromoacetylene and 4.7 cm³ of bromine, in a sealed tube at 165°C for two days. The products of the reaction were HBr and C₂HBr₅. Higher temperatures led to the formation of hexabromoethane. The resulting crystals were separated by compression between filter paper, dissolved in alcohol of 90°, and recrystallized by cooling. The purified compound melted at 56°-57°C and was insoluble in water and soluble in alcohol, ether, chloroform, and carbon disulfide.⁵⁰

In a following paper Bourgoin proved that the product of the reaction of bromine with tetrabromoethane was identical with that of the reaction of bromine on acetylene perbromide, that is, both were pentabromoethane.⁵¹

Chlorobromoethylene
Bourgoin reported that the reaction between acetylene perbromide and chlorine generated a new crystalline substance, which he proposed naming chlorobromoethylene chloride. This new compound had the same composition as perchlorethylene bromide. Chlorobromoethylene lost its bromine when heated in a closed vessel to 185°C; heated to 140-150°C with twice its weight of commercial aniline, it caused a violent action, resulting in the formation of a perfectly pure perchlorethylene. It also lost its bromine when treated with dilute sulfuric acid in the presence of zinc. Similarly, chlorobromoethylene chloride decomposed at 185°C, and free chlorine was again absorbed when the temperature was raised a little above this point. When heated with aniline it decomposed at about 100°C.⁵²

Transformations of pyrotartaric acid
Bourgoin reported that the reaction of a mixture of ordinary pyrotaartaric acid, bromine, and water, in a sealed tube for 26 hours at 132°C, produced CO₂ accompanied by an odorous, colorless liquid of density 2.93, which gave off irritating vapors. Its centesimal composition corresponded with the formula C₂H₂Br₄, and its chemical and physical properties were the same as those of tribromoethylene hydrobromide.⁵³

Similarly, treating 2 molecules of bromine with one molecule of pyrotartaric acid at 118-120°C for nine hours in a sealed tube, resulted in the formation of CO₂, HBr, and dibromosuccinic acid. This result proved that succinic acid and pyrotaartaric acid were true homologues. Heating 7.2 g of normal pyrotartaric acid, with 18 g of bromine and 15 cm³ of water to 100° for 90 hours, gave some dibromosuccinic acid, dibromopyrotartaric acid, and an oily liquid which, after purification by washing with caustic potash, crystallized from a mixture of alcohol and ether in crystals melting at 54-55°.⁵⁴

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