Rev. CENIC Cienc. Biol.; Vol. 53. (1): 043-055. Año. 2022. e-ISSN: 2221-2450.

REVISION BIBLIOGRAFICA

GUILLAUME DUBUC

Jaime Wisniak[a] (0000-0002-0265-4193)

* Department of Chemical Engineering, Ben-Gurion University of the Negev,Beer-Sheva, Israel 84105
wisniak@exchange.bgu.ac.il

Recibido: 3 de enero de 2022; **Aceptado:** 8 de enero de 2022;

ABSTRACT

Guillaume Dubuc (1764-1837), a French chemist and pharmacist who carried important research about opium, vegetable principles (jalap, aloe, ipecacuanha, squill, buckthorn, belladonna, madder, and pokeweed), distillation of seawater, active carbon, the apple aphid, and the use of calcium chloride for food conservation and as manure. He proved that commercial opium was not the pure extract or poppy juice and that the Levant opium was not the only extract prepared from white poppies. He defined the correct composition of the plant extracts described in the French Code, the procedure for identifying adulterants in madder, and suggested the use of the juice of pokeweed as a textile dye. Examined a large number of vegetables as possible sources of active carbon and classified them according to their water absorption capacity. He suggested using the apple aphid as replacement of cochineal. He proved that a dilute calcium chloride solution was appropriate for conserving meat and vegetables and also an active material for increasing the growth of plants.

Keywords: calcium chloride, opium, plant principles, phytolacca, seawater, tobacco.

RESUMEN

Guillaume Dubuc (1764-1837), químico y farmacéutico francés que investigó el opio, varios principios vegetales (jalapa, aloe, ipecacuanha, escila, belladonna, rubia, espino cerval, y la hierba carmín), la destilación del agua del mar, el carbón activo, el áfido del manzano y el uso del cloruro de calcio para preservar alimentos y como fertilizante. Demostró que el opio comercial no era el extracto puro del jugo de la amapola y que el opio oriental no era el único extracto o jugo obtenible de la amapola blanca. Definió la composición correcta de los extractos vegetales listados en el Codex francés, el procedimiento para identificar adulteraciones de la rubia, y sugirió el uso de la hierba carmín como colorante textil. Examinó una variedad de vegetales como posibles fuentes de carbón activado y los clasificó de acuerdo a su capacidad de absorber agua. Sugirió el uso de áfido del manzano como posible reemplazante de la cochinilla. Demostró que una solución diluida de cloruro de calcio servía para conservar carnes y vegetales, así como para aumentar el crecimiento de plantas.

Palabras clave: agua de mar, cloruro de calcio, opio, phytolacca, principios vegetales tabaco

INTRODUCCIÓN

Life and career (Avenel, 1839; Frère, 1857; Labat-Hacout, 1997)

Guillaume Dubuc was born in Sierville (Seine-Maritime) on January 29, 1764, the son of a family of farmers. He took his basic education as a boarding student at school in Fresquienne and Montivilliers; a relative of him, prosecutor of the commune of Montivilliers took him out of the boarding house and put him to work in his office, a job he disliked and abandoned to enter the pharmacy of M. Abraham as an apprentice. After two years, he transferred to the pharmaceutical laboratory of M. Carpentier in Rouen and eventually took over the business.

While in Rouen he took several courses at the Académie des Sciences de Rouen. Eventually he moved to Paris and began working with Sureu d'Emorette, one of the most illustrious pharmacists of his time, and in 1784 he returned to Rouen to work again with Carpentier. In1785, at the age of 22, he participated and won the competition for the position of chief pharmacist of the Hôtel-Dieu, without being in possession of a pharmacist diploma. This position allowed him to be nominated maître en pharmacie. The following year he was elected corresponding member of the Société de Médicine de Paris, the Société Libre des Pharmaciens, and the Société de Pharmacie de Paris, and begun a brilliant research career.

The British continental maritime blockade of France in 1809 led to scarcity and extreme price increase of the sugar imported from the colonies, with the corresponding hardship to the population. This led Dubuc and other French scientists to find procedures for manufacturing this critical foodstuff using local raw materials (apples and pears) (Dubuc, 1808, 1809, 1811). In 1829, the Institute of France (the future Académie des Sciences) awarded him the Monthyon Prize (category: making an art or craft less unsanitary; 3,000 francs and a gold medal) for his memoir about more hygienic methods for gluing fabrics using various types of facings (Dubuc, 1820, 1822a, 1829), and in 1832 the Société d'Encouragement gave him a bronze medal for having proposed a partial solution to the problem of determining the adulteration of flours with fecula of potatoes (Gaultier de Claubry, 1833; Dubuc, 1834a). Dubuc was member of the Académie Royale des Sciences, Belle-Lettres et Arts of Rouen (1809), founding member of the Société Centrale d'Agriculture du Département de la Seine- Inférieure (1819) and its President in 1829, the Conseil d'Agriculture Départamental, the Société de Médecine, the Conseil Centrale de Salubrité, and the Jury de Médicine de Rouen (1803-1830). He was corresponding member of the Académie Royale d Médicine, the Société de Pharmacie de Paris, the Société d'Agriculture, Sciences, et Arts du Département de l'Eure, the Société d'Agriculture et du Commerce de la Ville de Caen, the Société d'Agriculture de l'Aube, the Académie Ebroïcienne, etc. Dubuc passed away in Rouen (Seine-Maritime) on October 10, 1837, and was buried in the Saint-Gervais cemetery.

Scientific contribution

Dubuc wrote about 50 papers and books (i.e., Dubuc, 1829, 1837a) on the subjects of inorganic chemistry, organic chemistry, mineral chemistry, and toxicology. In addition to the subjects described below, he developed new methods for gluing fabrics using various types of facing (Dubuc, 1820, 1822a, 1829); he analyzed imported figs considered dangerous by the authorities (Dubuc, 1821a); extracted and described some of the properties of peanut oil (*Arachis hypogæa*) and discussed its possible commercial uses Dubuc, 1822b); analyzed the preparation of ciders and parries, their respective qualities and market price (Dubuc, 1824a);the preparation of potassium nitrate from vegetables, without the addition of animal matter (Dubuc, 1825a); the chemical and toxicological procedures for detecting poisoning by mercuric chloride and arsenic (Dubuc, 1825b); developed a simple process for the manufacture of paper from the stalks of potatoes (Dubuc, 1833); etc.

Opium

Dubuc wrote that the history of opium was little known. It was still uncertain if it existed in drops or if the people from the Orient extracted it from the opium poppy (*Papaver somniferum*). In the latter case, nothing was known about the extraction procedure and at what state of the plant. These divergences led him to study the problem in more detail (Dubuc, 1801). He discovered that at least one fourth of the Oriental opium consisted of impurities composed of finely divided particles of the stem, leaves, capsules, and seeds of the poppy. This admixture produced the peculiar narcotic odor of opium, which was very volatile, and particularly strong and nauseous in the internal tough parts of the plant. Dubuc believed that the presence

of this volatile fraction was merely accidental, an assumption (and others) he attempted to confirm by ten experiments conducted under different conditions, for example, (1) drying fresh and tough opium at 50° to 60 °C until it became pulverizable, resulted in the total loss of the narcotic odor, while retaining that of purified opium or laudanum (a tincture of opium containing approximately 10% powdered opium by weight), from which it only differed by the heterogeneous particles, which it contained. Collection of the volatile matter showed that it was totally soluble in water. Animals brought in contact with this matter were immediately suffocated. (2) Leaves of the white poppy, squeezed and triturated in a stone mortar, yielded a large quantity of a bitter milky brownish juice, which exposed to the air at 12.5 to 15 °C swelled considerably, giving a strong narcotic smell, similar to that exhaled by fresh opium. On the fourth day the exhalation had increased to such a degree that no person could smell it without a violent headache. Exposure to the sun, with stirring, the narcotic smell gradually diminished and was followed by another much resembling that of nitrogen. (3) Twelve pounds of poppy, almost fully grown, treated as in the previous experiment, were exposed to the air but not to the sun. Two days after, the whole mass began to ferment and release the narcotic odor. The juice, expressed, filtered, and evaporated to the consistency of an extract, did not produce true opium because the juice, as it was thickening, gradually lost the narcotic smell and only retained that of an odorless plant. (4) The juice of the young heads of poppy, partly taken from the plant in flower, was evaporated to half its quantity, hoping that a more concentrated mass would produce a substance retaining the odorous particles. This assumption was shown to be wrong. (5) A mixture of 368 grams of poppy heads, fully grown, but still green, and 113 grams of leaves and of the stem, were squeezed and perfectly triturated into a thick glutinous mass. On being exposed to the air the mass fermented and after a few days it smelled like opium. Part of it, evaporated at about 40 °C, retained a weak smell of laudanum, and resembled common opium. Dubuc took 0.065 grams of this substance and experimented a long and quiet sleep. (6) A large amount of poppy was boiled with water. Upon cooling, the extract became milky but did not smell like opium. It was evaporated to dryness and divided into two portions. One portion was mixed with enough juice from the fourth experiment to give it the consistency of common opium. The resulting mixture resembled laudanum in color, smell, and taste. The second portion was mixed with juice from the fifth experiment; after three days the mixture became so very similar to opium, that it might have been taken for good opium for its viscosity, color, and flavor (Dubuc, 1801).

Dubuc concluded as follows: (a) commercial opium was not the pure extract or the juice extracted from the stalks, leaves or green poppy capsules, because it contained a large percentage of impurities, equally distributed in the mass; (b) the juice or the extract prepared by heating did not have the volatile odor characteristic of Oriental opium; (c) the Oriental opium was not the only extract prepared by washing or decoction of white poppy heads; (d) it seemed that the opium of the Levant was the dried extract of any species of white poppies, taken between the moment of their flowering and the moment of their maturity, then mixed and reduced to the known consistency, with the volatile mass coming from the stems, leaves, green capsules of these same poppies, crushed and fermented until the moment when the volatile obnoxious odor developed. This mass was then divided in rolls, wrapped and kneaded on their surface with poppy leaves partially desiccated and then sent abroad (Dubuc, 1801).

Plant principles –Extracts

Dubuc wrote that the French dispensary manuals gave a very vague definition of the concentration of the alcohol used to extract resinous and extractive vegetable principles. As a result, pharmacists interpreted terms like *rectified spirit of wine*, or *spirit of wine*, arbitrarily. Some used alcohol of 18° Bé (relative density 0.946), others of 32^0 (0.864), 36^0 (0.843), or 38^0 (0.833), etc. with the resulting confusion when interpreting the results (Dubuc, 1803). For this reason, he decided to study the preparation of five important substance of medical importance (jalap, aloe, ipecacuanha, cinchona, and squill) and their influence when using alcohol of 38, 32, 26, and 20° Bé degrees of strength (which Dubuc numbered 1, 2, 3, and 4).

(1) Jalap. Extracts obtained by macerating 7.20 cm^3 of resin with 15.6 g by of alcohol, turned milky by addition of water, and yielded after careful evaporation:

No.	Product
1	0.388 g of pure resin
2	0.324 g of resin and 0.065 of gum
3	0.518 g, of which about 50% of gum
4	0.453 g, of which 0.259 g of gum

These results indicated that that in order to prepare the resin of jalap, and also a tincture as strong as possible, it was necessary to employ alcohol of 36^0 Bé (density 0.843). This tincture should be denominated the *alcoholic resinous tincture of jalap.* Dubuc added that a less active resino-gum tincture, prepared with No. 3, might be kept in the shops under the name *vinum jalapii* (Dubuc, 1803).

(2) Aloe. Before submitting this substance to the action of the graduated alcohols, Dubuc tried it with cold water. Treatment of 7.80 g of aloe succotrina with 42.5 g of water extracted 3.89 grams of gum of an insupportable degree of bitterness; the remainder was dissolved in alcohol of 36^0 Bé, and furnished, by evaporation, a resin much less bitter than the extractive matter. The different alcohols extracted as follows:

No.	Product
1	5.83 g of resin and 1.94 of gum
2	5.18 g, of which 2.33 of resin
3	3.89 g, of which 1.30 of resin
4	3.29 g, of which 0.65 g of resin

From these results, Dubuc recommended the preparation of two spirituous tinctures to be kept in the shops, the first made with the raw aloes and with alcohol of from 36^o to 38^o Bé, to be called the *alcoholic tincture;* the second, with alcohol of the same degrees of strength, but with the aloes deprived of its extractive matter by means of water. This might be termed the *alcoholic resinous tincture* of aloes (Dubuc, 1803).

(3) Ipecacuanha. Dubuc described the precautions to be taken in the pulverization of the root and the need to keep it in small and well-closed bottles. His results were as follows:

No.	Product
1	0.583 g of pure resin
2	0.648 g, of which 0.518 of resin and 0.130 of gum
3	0.778 g, of which 0.324 of resin and 0.454 of gum
4	0.907 g, of which 0.324 g of resin and 0.583 of gum

According to Dubuc, the last tincture seemed to contain the principal virtues of the root and hence, should be administered as potion. It was also appropriate for making *vinum ipecacuanha*, and for the preparation of syrup (Dubuc, 1803).

(4) Cinchona *rubra and grisea.* Extraction of 3.70 g of bark with 28.35 g of each of the four alcohols yielded as follows:

No.	Product
1	0.518 g of resin and 0.065 g of gum
2	0.454 g of resin and 0.194 of gum
3	0.389 g of resin and 0.389 of gum
4	0.389 g of resin and 0.389 of gum

Based on these results Dubuc suggested two recipes, giving preference to the one made with the weakest alcohol, and which he deemed the most proper for preparing a *vinum cinchona* (Dubuc, 1803).

(5) Squill. Dubuc recommended that this substance be also kept it in small and well-closed bottles. He extracted 3.88 g of dry squill with 1.55 g of each alcohol, evaporated 15.55 g of each tincture, and obtained the following results:

No.	Product
1	0.518 g, of which 0.194 g resin and 0.324 g of gum
2	0.583 g, of which 0.194 g of resin and 0.359 g of gum
3	0.777 g, of which 0.130 g of resin, 0.518 g of gum, and the rest extractive matter
4	0.907 g, of which 0.130 g of resin, 0.518 g of gum, and the rest extractive matter

The last tincture appeared to be the most fully impregnated with the different principles of the squill and hence, recommended to prepare the *vinum scilliticum* and also an extract by evaporation, likewise well fitted for mixing with the *miel scilliticum* (Dubuc, 1803).

This paper ended with the formulation of four new recipes for the liquid laudanum of Sydenham (opium combined with sherry), tartar emetic, the butter of lead (a mixture of olive oil, fat, and lead acetate), and the *unguentum nutritum* (ointment of litharge of gold, olive oil and vinegar) (Dubuc, 1803).

Acetic acid

In 1801 Badollier reported a new method for preparing acetic acid based on heating over a sand bath a glass balloon containing a mixture of 907.2 g each of cupric sulfate and lead acetate. According to the author, the acid thus prepared was identical in quantity and properties to the one prepared directly from lead acetate, but at a cost of only 25% and without the bad taste communicated to the latter by the acid that decomposed during the reaction (Badollier, 1801). Dubuc repeated the Badollier process using a distillation apparatus that allowed heating the mixture at increasing temperatures and collecting any product released (Dubuc, 1805). The acid obtained seemed to have an opposite effect to the one obtained from lead acetate alone. This result led Dubuc to repeat the experiment, carefully observing the changes taking place during the reaction. He noticed that the mixture became pasty and yielded 737 g of distillate composed of 113.4 g of water, slightly acidified, 113.4 g of a liquor acider than the first portion and similar to a good Saumur vinegar, and 513. 3 g of a limpid liquor smelling like a mixture of acid and sulfur dioxide. The distillation residue was 1077.3 g of a solid composed of several red colored layers. Dubuc assumed that the reaction involved production of SO_2 and decomposition of the sulfuric acid by the transport of its oxygen to the vinegar; an effect contrary to the affinity of the acid for acidifying and solidifying bases that generated a super oxidized acetic acid. Dubuc eliminated the impurities present in the third fraction by simple adding to it 0.13 g of tartar and 57 g of manganese dioxide, leaving the mixture alone for 24 hours, followed by distillation. The resulting vinegar was almost identical to the one obtained from lead acetate (Dubuc, 1805).

The pertinent publication contains the report of the committee appointed by the Société de Pharmacie de Paris [Louis Antoine Planche (1776-1841) and Pierre François Guillaume Boullay (1777-1869)] to evaluate the results reported by Dubuc. Boullay and Planche repeated Dubuc experiment, adding to the distillation flask two washing bottles in series, one containing distilled water, and the other limewater, followed by a vessel for capturing any gas released. They obtained 226.8 g of a liquid similar to distilled vinegar, although of weaker odor, 283.5 g of a liquor smelling less agreeable and more penetrating than acetic acid, and not containing SO_2 or SO_3, and 198.4 g of another very limpid liquid, having a piquant smell and not precipitating barium chloride. In addition, they collected 5.51 g of CO_2 and a distillation residue composed of several layers of different colors. The resulting acetic acid was almost identical to the one obtained from lead acetate (the same result reported by Dubuc). The committee disagreed with Dubuc's assumption that acetic acid was super oxygenated vinegar generated by the transport of oxygen from sulfuric acid to the vegetable acid. They based their opinion on the results reported by Darracq that there was no difference between acetous acid (old name given to ordinary vinegar, assumed to differ from concentrated acetic acid by one degree less of oxygenation) and acetic acid and that the apparent differences were due to impurities of mucilagous matter. There existed only one vinegar acid, present at its maximum degree of oxygenation (Darracq, 1802; Dubuc, 1805).

Buckthorn purgative (Nerprun, *Rhammus cathartica*)

According to Dubuc, notwithstanding the advances of pharmacy in the last 15 to 20 years, there were still important medicines that their components and proportions, and their method of preparation, were not clearly defined to assure a constant effect. The syrup of Nerprun was one of such medicines; its preparation

was not clearly defined so as to warrant its purgative effects. No one had reported the result of experiments that allowed determining the appropriate state of its juice, maturity of the beans, fermentation, etc., to assure its maximum potency (Dubuc, 1812). Many pharmacists had mentioned this inconvenience, particularly Nicolas Deyeux (1744-1837). Deyeux had mentioned the significant differences that existed between the syrup prepared by different pharmacies in different places of France, the frauds in its composition, and the alterations produced by the accompanying components. To clarify these points, he extracted the juice from ripe and non-ripe berries and noticed that their color and taste were so different that it could not be that they gave identical syrups. In practice, this was so: the syrup prepared from ripe berries was more purgative than the one prepared from non-ripe berries. Deyeux also prepared the syrup with juice obtained from fresh berries and from berries that had begun to ferment. Once again he noted a significant difference: the second type of berries produced a stronger purgative. These results led him to dispense in his pharmacy only buckthorn syrup prepared only with fermented juice. To his judgment, this syrup provided constant effects (Deyeux, 1797).

Dubuc added that his experience indicated that the strength of the syrup varied also with the proportion between juice and sugar. For example, the *Codex Medicamentarius Seu Pharmacopea Parisiensis* (1760) prescribed the use of three parts of pure nerprun juice and two parts of a sweet principle, while the *Pharmacopée de Lémeri* (1728) recommended mixing the nerprun juice with sugar, honey, cinnamon, and mastic (a resin obtained from the mastic tree, *Pistasia lentiscus*). Dubuc described the properties of the juice obtained from berries and sold in the local shops, generally picked before maturity, from the berries collected from the same trees 12 days later, and from those picked towards the end of the season, when the berry would fall alone with the slightest wind. In the latter condition, the berries had a shining black color, their seeds separated from the parenchyma by a slight pressure, and the juice (50% of the weight of the berry) was clearly bitter but not acrid. According to Dubuc, this was the berry that should be used in pharmaceutical preparations. This juice was also the one appropriate for preparing buckhorn green (a watercolor used for painting landscapes). This type of berries could be dried and kept for many years, and used for preparing syrup or buckhorn green. For this purpose, it was enough to macerate them for 24 hours with double their weight of boiling water (Dubuc, 1812).

Belladonna (Atropa belladonna)

Dubuc wrote that the Solanaceae, particularly belladonna, produced a large quantity of poisonous fruits. The belladonna berries were all the more to be feared, especially for young people, as their external look and shape tempted to eat them, and presenting when ripe, the appearance of a small cherry or a large black grape. Not only the fruits were poisonous; the deleterious principles they contained were soluble in wines and alcoholic liquors making them pernicious (Dubuc, 1815).

Years before, a physician had requested Dubuc to examine an adulterated wine that produced drunkenness even when taken in small dose. This condition was followed by total destruction. This drink was quite pleasant to the taste; never the less it left the tongue with a particular harshness, which signaled the presence of a foreign body. Dubuc carried a series of tests that showed that this wine did not contain mineral substances, particularly lead salts. These results, the effects on the human body, its particular taste, and its beautiful amaranth red color, led him finally to assume that the pernicious effects were due to the presence of a vegetable substance belonging to the papaveraceae or solanaceae family. Testing for opium or its preparations produced negative results. Wine mixed with opium, even on a large dose, presented a dark cloudy color and a taste far from that of good ordinary liquor. Similar experiments with seeds of *Datura stramonium* yielded similar results. Eventually, Dubuc was led to the mature berries of belladonna and the possible ways of identifying its deleterious components (Dubuc, 1815).

Dubuc described the juice of belladonna as a viscous liquid, initially slightly sweet and then bitter, acrid, and styptic. Five or six berries, crushed and macerated over the tongue, produced a temporary paralysis of the organ, which could be interrupted by washing the mouth with water acidulated with lemon juice or vinegar. The juice was not basic and not acid, and did not affect litmus paper or tincture of violet petals, but turned red or green with acids and alkalis. Dissolved in three or four volumes of water produced a blood red solution, which eventually became turbid and white, as long as kept in a closed vase. Alcohol dissolved completely a resinous substance, producing a violet red solution, having a piquant, acrid and

bitter taste. Addition of a large volume of water precipitated white flakes containing the styptic component (Dubuc, 1815).

Treating the dry berries with alcohol extracted a yellow coloring substance, while treatment with ether produced a green solution. Evaporation of the latter left a thick liquid, oily, green, acrid, and strongly styptic. All these results led Dubuc to assume that this matter contained the poisonous principle of belladonna. Additional tests indicated that detection of the styptic effect in one liter of wine required the dissolution of the juice of at least 24 to 30 berries. Mixing a wine contaminated with belladonna, with ten to twelve times its volume with pure water, turned a red wine, dull and opaque, and white brown, a white wine. The berries also colored brandy and other alcoholic drinks (Dubuc, 1815).

Dubuc summarized his findings as follows: (1) well-mature berries of belladonna had, initially, a slightly mucous taste that change to acrid, styptic, and slightly bitter; (2) white or red wines dissolved the poisonous principles of belladonna without visible changes; mixing them with different proportions of water resulted in color changes and precipitation of deposits. These effects did not appear with pure wines; (3) highly pure alcohol extracted from the fruits of belladonna a violet red dye; (4) the dry berries tinted alcohol yellow, instead of violet red; and (5) ether extracted from belladonna a green oily principle, highly styptic, which possessed the poisonous properties of belladonna (Dubuc, 1815).

Madder (Rubia tinctorium)

Dubuc wrote that if madder were used in its natural state, that is, without being ground in the dyeing workshops, falsification would become almost impossible since its root had a physical aspect and a sweet sugar taste different from all other vegetable material. In practice, it was otherwise; the root was sold commercially in a powdered state, enclosed in large masses in the barrels where it heated up and acquired brownish color, analogous to that of the bark used to adulterate it. This bark came from coastal regions of North Africa via Marseille and was also known as *pine* or *false madder*. Red ochre and ferruginous clay were also used for this purpose. Dubuc proceeded then to describe the methods employed for identifying the ingredients employed for falsifying madder (Dubuc, 1831a).

1. Ochre and other terreous materials

About 60 g of the suspected material are mixed with enough water and agitated for about one minute. The mass is left to rest and the operation repeated for a second time. Any ochre or clay precipitates to the bottom. It is separated and dried; its weight indicates its proportion in the starting material (Dubuc, 1831a).

2. False madder

True madder is resinous and does not contain an appreciable amount of gallic acid or tannin, while false madder contains large amounts of these substances. This property allows differentiation by means of ferric acetate or alcohol.

(a) About 60 g of the ground root, or of commercial root, are macerated with two glasses of boiling water. The filtrate is split into two parts; one is treated with ferric acetate, the other, with a concentrated solution of aqueous glue. If false madder is present, the first portion will turn black and the second will precipitate gelatin tannate, colored gray white.

(b) One portion of 120 g of the suspected material is brewed with 60 g of wine spirit. The operation is repeated with 60 g of bark or of false madder. Both will produce a red solution. In the first case, appearance of turbidity will indicate precipitation of the resin of madder; ferric acetate will not react. The tincture of false madder will not become turbid and ferric acetate will produce a black color (Dubuc, 1831a).

Pokeweed (Phytolacca Decandra)

According to Henri Braconnot (1780-1855) pokeweed was an acrid plant with a very thick fleshy root and very high purple stalks. He calcined the stalks and found that the ashes contained calcium and potassium, both combined with an undetermined acid. Boiling the stalks with water produced liquor that did not react with litmus paper. Evaporation to a syrupy consistency deposited a salt, which was mostly soluble in water. The remaining white solid dissolved in nitric acid and with lead nitrate produced a copious precipitate, while the filtrate afforded an abundant crystallization of potassium nitrate. Braconnot tested the salt with a

variety of reagents and concluded that the acid present in pokeweed was probably an acid between malic and oxalic acid or an oxygenated malic acid (Braconnot, 1807).

Braconnot also examined the coloring matter present in the berries of phytolacca. Ground with water in a mortar yielded a fine bright purple liquid, sweet and acrid, which tinted litmus blue, and at moderate temperatures underwent alcoholic fermentation. The resulting wine had an unpleasant taste. Treatment with a few drops of limewater turned it yellow, but addition of a small amount of acid, including hydrogen sulfide, restored the original purple hue. Braconnot postulated that this yellow liquid seemed to be a very delicate test of the presence of acid, probably four times as sensible as the infusion of litmus. Additional tests of the purple liquid indicated that caustic alkalis turned it yellow and alkaline bicarbonates, violet. Ferric sulfate produced a dirty red precipitate and tin chloride a lilac one, Weak acids and calcium chloride had no action. The purple color that tinged the epidermis of the stalks was of the same nature as the one contained in the berries. Braconnot added that in North America the leaves were boiled and eaten as spinach. The juice of the root was purgative and should not be used when there is any inflammation of the viscera (Today, the primary toxic compounds of pokeweed are thought to be oxalic acid, saponins (phytolaccotoxin and phytolaccigenin), and an alkaloid (phytolaccin).) (Braconnot, 1807).

Frédéric Kuhlmann (1803-1881) tried using as a dye the beautiful purple color of pokeweed berries. He reported that acids, dilute or concentrated, did not enhance the color of the juice even after a long time. Weak alkalis made it violet, while concentrated alkalis destroyed it completely after a few hours. Initially, ferrous sulfate changed the color of the juice from purple to violet but destroyed it after prolonged exposure, probably because the salt took the oxygen of the dye, became oxidized and destroyed the coloring matter. Kuhlmann tried without success to apply the color to linen, cotton and wool, independently of the mordant used. The process was possible with silk treated with alum or tin mordant; in the first case the silk acquired a hydrangea hue and in the second, dark violet. These colors were very resistant to chemical reagents and could be considered as solid and most appropriate for dying silks; the only precaution to be taken was to avoid a boiling temperature because it changed the color to brown (Kuhlmann, 1826-1827).

Dubuc considered that the possible use of the different parts of the plant as dye had not been studied enough, particularly the fact that the color of the leaves changed with the age of the growth (green in July, red green in September, and red in November). Consequently, he conducted a series of experiments with the leaves and the berries and reported the results of nine of them, four with the leaves and five with the berries (Dubuc, 1831b).

The leaves of each group (1, 2, and 3) were brewed in water for 15 minutes and the decoction allowed to cool and then poured with expression. Liquor 1 had a strong olive yellow color; it was bitter and styptic, and smelled strongly. Left in the air it turned black brown. Liquors 2 and 3 were red, more bitter and styptic than liquor 1, and blackened strongly in the presence of light and air. The three liquors were odorless and did not react with violet and litmus tinctures. They were colored by ferrous sulfate and acetate as follows: 1, brown black; 2, violet black; and 3, intense black. A strong glue made them muddy in the order 1 > 2 > 3. All these results proved, chemically, that the leaves changed their color according to their content of tannin and gallic acid (Dubuc, 1831b).

The green and red leaves, cooked in a solution of commercial sodium carbonate, generated a dark yellow solution that tinted clear brown linen and cotton yarn previously mordanted green leaves tinted wool yellow gold, when degreased and mordanted with tin chloride. The liquor of the red leaves was very rich in gallic acid; it tinted dark black wool, when degreased and imbued in ferrous salts. Dubuc also found that the dry red leaves, mixed with the proper additives, could be used to prepare black indelible ink (Dubuc, 1831b).

Dubuc described in detail the use of the juice of pokeweed in tinctures and the arts, and concluded as follows: (1) the leaves, red better than green, tinted tissues yellow, fawn, purple, etc., when mordanted with ferruginous salts and other terreous and metallic mordant; (2) depending on the mordant, the berries tinted cotton and wool yarns with various solid colors, and also produced an economical rouge, which could replace ordinary carmine without disadvantage; and (3) the red leaves and the berries could be used for manufacturing a cheap ink, or better indelible ones, when mixed with gallnut, wood of India, or other astringent ingredients (Dubuc, 1831b).

Dubuc concluded his paper with information about the proper way of cultivating pokeweed for commercial purposes (Dubuc, 1831b).

In another paper Dubuc described his efforts for using the leaves of pokeweed, beets, and potato, for manufacturing a substitute for tobacco, free of nicotine and its toxic properties. His colleagues thought that his efforts were the same as trying to prepare wine without using grapes (Dubuc, 1834b). He first described the composition of the brine used by tobacco manufacturers for sprinkling the leaves of the tobacco plant during their processing. Basically, this brine contained, by weight, 32% of common salt, 64% g of brown sugar, and 4% of calcium chloride, plus one liter of pure water per kilo of solids. The leaves of pokeweed were taken at the three stages of their growth, while those of the beets and potatoes were collected in spring or in autumn, according to their nature (Dubuc, 1834b).

At the end of June, Dubuc collected a large quantity of pokeweed leaves and dried them until they lost 75% of their natural humidity. They were then pulverized, slightly sprinkled with the brine, and put back in a pile and always in the shade. Soon they warmed up and fermented; they were now finely divided again, sprinkled a second time with the brine, and kept in small batches in a dry place. In the following months these leaves converted into tobacco, quite analogous, in taste, amount and odor, to the one prepared with nicotianas. Dubuc exhibited a sample to the members of the Académie de Sciences. He repeated this process with leaves collected in August and October; the August leaves produced the same result as those collected in June, while the October ones produced a tobacco of good odor but somewhat weaker. Similar results were obtained with the leaves of beets and potatoes (Dubuc, 1834b).

Dubuc wrote that his results proved that it was possible to manufacture in large amounts a tobacco substitute from the leaves of pokeweed, beets, and potatoes, with clear health and economic advantages. The use in France of the leaves pokeweed, as nicotiana substitutes for making tobacco, would limit the cultivation of this last plant, and the wheat lands would become less crumbled “because tobacco was one of the plants which purified the most, and in a short time, the most fertile soils used regularly for the growth of edible plants”. The cultivation of beets, less land-consuming than tobacco, would increase in the countryside without damaging too much the harvesting of cereals, an advantage which was not to be scorned in a country with a large population (Dubuc, 1834b).

Distillation of seawater

Dubuc wrote in 1821 that the Académie des Sciences de Rouen had requested from him to evaluate three booklets they had received from M. Lesage in which he postulated that distilled seawater contained always “an inherent alkaline gas, which could not be eliminated by repeated distillation. This gas made water unhealthy, morbid, etc.” Three committees had previously studied this report and concluded that “seawater, no matter how carefully distilled, always kept a weak maritime or marsh odor”. This odor was attributed to the caloric, which the water lost after 10 to 20 days and then became very pure. The referees dare not too strongly to assert the safety of distilled seawater and contented themselves to declare that this water could, without harming health, be used for drinking and the necessities of life, at least for one month (Dubuc, 1821b).

Dubuc carried a series of experiments using glass equipment to avoid contaminating his samples of seawater. He distilled the water and collected three fractions. The first one had a relative density very similar to distilled pure water. At room temperature it was limpid and diaphanous but became shady when cooled to 6.2^{o} to 7.5 ^{o}C; it recovered its limpidity upon heating. It had a brackish and piquant taste but upon cooling, it eventually lost these properties, while precipitating a small amount of flaky matter. The second fraction was inodorous and tasteless and did not lose its transparency when cooled to 6^{o} or 7 ^{o}C. It turned green the violet tincture but lost this property on addition of a few drops of acetic acid. It became slightly muddy on addition of mercuric chloride, showing that it contained a very small amount of an alkaline matter. Hence, it could not be considered distilled water. The third fraction was odorless and tasteless, did not act on the tincture of violet and dissolved soap easily. It had all the properties of water distilled from a well or a river. All these results confirmed the claim of Lesage that *non-fractioned* distilled water was unfit for drinking because it contained a certain amount of an acrid principle. Nevertheless, Dubuc decided to extend his study and search for an easy way to obtain drinkable water by *fractional* distillation of seawater, since his results pointed to the quality of the second fraction distilled After additional experiments, he developed the following procedure, which he considered economical and easy

to perform: 100 liters of seawater were mixed with 250 g of concentrated sulfuric acid (relative density 1.836) and distilled under temperature controlled conditions (up to 100°-110 °C). The first 50 liters were rejected and the following 50 kept (Dubuc, 1821b).

Active carbon

Dubuc wrote that present knowledge taught that the pyrolysis of vegetable substances left a residue that was extremely powerful in neutralizing obnoxious gases, absorbing water, bleaching aqueous and alcoholic solutions, eliminating vegetable colorants, etc. This type of carbon was also used in medicine for curing bad breath, treating certain gangrenous abscesses, drying ulcers and wounds, and eliminating ringworms. To assume that the active carbon obtained from all species produced equal and constant effects implied assuming that their composition was essentially the same. Dubuc believed this assumption was wrong; the carbon constitution and properties had to depend on the nature of the tree, the season, its age, habitat, climate, etc. For these reasons he decided to compare the different carbons on their ability to retain water. For this purpose, he chose four carbons prepared from light white or slightly tight grain wood (silver birch, hazel, white willow, and aspen), carbons harder and less spongy than those of the first group (beech, ash, pear, and apple), carbons obtained from even heavier woods (oak, horn beam, elm, and guaiacum), and carbons prepared from gums (Arabic, Senegal, tree exudations, etc.).

All the samples were odorless, tasteless, did not color alcohol, oils, and water, they burned without smoking, and were lighter than water. The samples were submerged in water until total saturation, dried by distillation, and the recovered weight registered (Dubuc, 1817).

Dubuc found that at the beginning of the submersion, the samples effervesced noisily, a phenomenon due to the release of the air and gases retained by the dry carbon. The more the sample was divided, the larger the amount of water it absorbed. Pulverized carbon did not present this phenomenon. All the samples communicated to the water a slight bluish hue, easily discerned in the presence of a strong light. Dubuc believed it was caused by fine carbon particles suspended in the liquid. In the long run, these particles settled and the water became diaphanous again (Dubuc, 1817).

The results indicated that the carbons could be divided into four classes, depending on the amount of water they absorbed: (1) light carbons, porous and spongy, represented by those originating from gums and absorbing three times their weight in water; (2) carbons originating from white trees, such as willow, poplar, silver birch, aspen, etc., absorbing twice their weight in water; (3) carbons prepared from beech, ash, apple, etc., absorbing 1.5 times their weight in water; and (4) carbons from very compact trees, and heavier than the previous classes, such as oak, elm, and guaiacum, absorbing 25% their weight in water (Dubuc, 1817).

Woolly apple aphid (Eriosoma lanigarum)

In 1826 Dubuc demonstrated that the woolly apple aphid presents in apple trees, contained a coloring substance analogue to the carmine provided by the cochineal, which was imported at high cost from Mexico. He believed that this insect, which resisted a cold of 12.5 °C, could be also be grown in the temperate zone, not on the apple tree but on other cheaper vegetables such as poppy, beet, and pokeweed, to serve as dye (Dubuc, 1826).

Dubuc also recommended two procedures to get rid of the insect: (1) Towards the end of June, to cut and burn the young branches and shoots where the insect was stationed and multiplied, and (2) to imbibe with a brush the chancrous parts of the tree where the insects accumulated during the fall, with a solution of 227 grams of cupric sulfate and 114 grams of sulfuric acid in one liter of water. One application was good enough to eliminate the pest (Dubuc, 1826).

Uses of calcium chloride

Conservation of foodstuff

Dubuc wrote that several scientists had already reported the possible use of several chemicals as a preservative for animal and vegetable matter, or as an antiseptic in certain cases (Dubuc, 1824b). In 1802, Chaussier had written that solid and fleshy spoils from animals could conserved with mercuric chloride (Chaussier, 1802). Others had added that gaseous substances such as SO_2, hydrogen fluoride, and oxygen allowed preserving fresh meat without decomposition or putrefaction. Also, that ordinary water, saturated

with aluminum acid sulfate and alcohol of 35°, served to conserve dead meat, but this claim had been rejected after finding, in many cases, that the meat had become unrecognizable. Afterwards, the main salting shops had reported that common salt, mixed with about 7% of calcium chloride, was more penetrating and more appropriate for the salting of meat and fish that pure sea salt. Dubuc added that his experiments had shown that aqueous solutions of calcium chloride were a cheap and effective medium for conserving animal spoils and certain vegetables (Dubuc, 1824b).

Dubuc wrote that all his experiments had been conducted with solutions containing 14 to 16% wt. of calcium chloride. In one of his experiments he had submerged 500 grams of fresh beef meat, fat and lean, in his saline solution and kept the whole in a glass jar, closed with a cork, for two years, at room temperature. The meat had retained its original shape and shown no signs of putrefaction, except for the release of a few lumps of fat that floated in the liquid. In another experiment he had submerged eight vipers in the same solution, and after seven years, observed that the vipers had kept their form and primitive color, without showing any sign of putrefaction. He had also submerged in the antiseptic liquid meat and fish showing the beginning of putrefaction and noticed the stop of fermentation. Dubuc reported that his solution was also able of stopping alcoholic fermentation: Mixing thirty liters of water, sweetened with honey or gross sugar, in clear fermentation, with 32 grams of calcium chloride resulted in the immediate stoppage of bubbling (Dubuc, 1824b).

Manure

Dubuc wrote that during the years 1820 and 1821 he had successfully tested the use of the same solutions of calcium chloride (see above) as a manure, particularly for textile plants such as flax (*Linum usitatissimum*) and hemp (*Cannabis sativa*) (Dubuc, 1827). Years before, he had communicated his first results to his colleague Pierre Lemaire-Lisancourt (1783-1841), which he reported in 1825 (Lemaire-Lisancourt, 1825). According to Lemaire-Lisancourt, Dubuc sowed some Indian corn in a light soil, watered six or eight days before with the calcium chloride solution, and also used for watering the plant during its growth. As a control, Dubuc planted at a distance of two meters, but in the same soil, maize, which he watered with common water. At maturity, the plant watered with the solution of the chloride, grew to double the size of the second. Dubuc found the same results with a variety of vegetables such as lilac, ordinary and fruit trees, onions, poppies, sunflower, and potatoes. He found that the potatoes treated with calcium chloride gave tubercles 15 cm long, 30 cm in circumference, and weighing nearly one kilo each; the ones produced with ordinary water were generally about half that size (Lemaire-Lisancourt, 1825).

In 1827 Dubuc published some additional results for flax and hemp (Dubuc, 1827). In this experiments he watered the ground with the calcium chloride solution, sowed the seed, and during the growth, watered the plants several times with the solution. Simultaneously, he conducted a parallel process using only ordinary water. At maturity he noticed that the plants treated with the solution had grown about 33% more than those treated with ordinary water, and were also stronger. He repeated these experiments in other types of soil and seasons, and observed the same results. In addition, he wrote that the seeds from the plants fertilized with calcium chloride were clearly more appropriate for the reproduction of the species than the ones obtained from plants treated with ordinary water (Dubuc, 1827).

BIBLIOGRAPHIC REFERENCES

Avenel, P. A. (1839). Notice sur la Vie et les Travaux de Guillaume Dubuc, Chimiste à Rouen. *Précis Trav. Acad. Sci. Rouen*, 171-199.

Badollier, M. (1801). Nouvelle Manière de Préparer l'Acide Acétique. *Ann. Chim., 37*, 111-112.

Braconnot, H. (1807). Sur le Phytolacca. *Ann. Chem., 62*, 71-90.

Chaussier, M. (1802). Note on a Method of Preservation of Animal Substances from Putrefaction. *J. Roy. Inst., 1*, 227.

Darracq, M. (1802). Observations sur les Acides Acétique et Acéteux. *Ann. Chim., 41*, 264-281.

Deyeux, N. (1797). Observations sur la Manière de Préparer le Syrop de Nerprun. *J. Soc. Pharm., 1*, 90-91.

Dubuc, G. (1801). Sur l'Opium et sur sa Composition. *Ann. Chim., 38*, 181-195.

Dubuc, G. (1803). Expériences sur le Jalap, etc. *Ann. Chim., 46*, 18-35.

Dubuc, G. (1805). Sur l'Acide Acétique. *Ann. Chim., 54*, 145-155.
Dubuc, G. (1808). Sur le Sucre Liquide Extrait du Suc de Pommes et de Poires. *Ann. Chim., 68*, 113-133.
Dubuc, G. (1809). Sur le Sucre Liquide Extrait du Suc de Pommes et de Poires. *Ann. Chim., 71*, 163-188.
Dubuc, G. (1811). Considérations ou Notes Générales Faisant Suite aux Mémoires Publiés en 1809 sur le Sucre Extrait des Pommes et des Poires, sur ses Appropriations à l'Économie Rurale et aus Besoins de la Vie, comme Supplément au Sucre Étranger. *Ann. Chim., 77*, 151-160.
Dubuc, G. (1812). Mémoire sur les Baies, le Suc et le Sirop de Nerprun (*Rhammus Catharticus*). *Précis Trav. Acad. Sci. Rouen, 68*, 13-15.
Dubuc, G. (1815). Note sur quelques Propriétés Chimiques des Baies de la Belladone (*Atropa belladonna*), avec des Moyens Proposés pour Reconnaître les Principes Délétères de ces Fruits, dans les Vines, Liqueurs, etc. *Précis Trav. Acad. Sci. Rouen*, 50-58.
Dubuc, G. (1817). Mémoire sur quelques Propriétés Comparées de Diverses Espèces de Charbons. *Précis Trav. Acad. Sci. Rouen*, 84-98.
Dubuc, G. (1820). Mémoire sur l'Encollage des Étoffes ou Toileries au Moyen de Diverses Espèces de Parements. *Précis Trav. Acad. Sci. Rouen*, 65-79.
Dubuc, G. (1821a). Notice sur des Figues Reconnues Dangereuses. *Précis Trav. Acad. Sci. Rouen*, 40-41.
Dubuc, G. (1821b). Sur la Distillation de l'Eau de Mer. *Précis Trav. Acad. Sci. Rouen*, 100-110.
Dubuc, G. (1822a). Parements ou Encollages pour les Étoffes et Toileries. *Précis Trav. Acad. Sci. Rouen*, 71-81.
Dubuc, G. (1822b). Sur le Pistache de Terre (*Arachis Hypogaea*). *J. Pharm., 8*, 231-235.
Dubuc, G. (1824a). Mémoire sur la Préparation des Cidres et Poirés, sur les Qualités Respectives, leur Prix Marchand, etc. *Précis Trav. Acad. Sci. Rouen*, 51–73.
Dubuc, G. (1824b). Sur les Diverses Propriétés du Chlorure de Calcium et du Muriate de Chaux Ordinaire Employés à la Conservation des Chairs Mortes de Certain Végétaux. *Précis Trav. Acad. Sci. Rouen*, 84–92.
Dubuc, G. (1825a). Mémoire sur la Fabrication du Salpêtre (Nitrate de Potasse) au Moyen des Végétaux et sans Addition de Matières Animale. *Précis Trav. Acad. Sci. Rouen*, 26–27, 151-174.
Dubuc, G. (1825b). Notice Chimico-toxicologique, tant sur le Sublimé Corrosif que sur l'Arsenic Ordinaire, faisant suite à un Rapport fait à la Cour d'Assises de Rouen, le 23 Novembre 1824, sur une Omelette Empoisonnée. *Précis Trav. Acad. Sci. Rouen*, 43–54.
Dubuc, G. (1826). Extrait de Deux Notices sur le Puceron Lanigère. *Précis Trav. Acad. Sci. Rouen*, 83–85.
Dubuc, G. (1827). Notice sur l'Emploi du Chlorure de Chaux en Agronomie. *Précis Trav. Acad. Sci. Rouen*, 43–55.
Dubuc, G. (1829). *Traité sur les Parements et Encollages dont l'Emploi Permet aux Tisserands de Travailler Ailleurs que dans les Caves et autres Bas-Fonds non Éclairés et Généralement Malsains*. Periaux, Rouen.
Dubuc, G. (1831a). Sur la Garance, avec des Moyens Simples d'en Reconnaître la Falsification. *Précis Trav. Acad. Sci. Rouen*, 46-49.
Dubuc, G. (1831b). Mémoire sur le *Phytolacca Decandra*. *Précis Trav. Acad. Sci. Rouen*, 57-81.
Dubuc, G. (1833). Notice sur du Papier Fabriqué avec des Tiges de Pomme de Terre Rouies par un Procédé Simple. *Précis Trav. Acad. Sci. Rouen*, 57-81.
Dubuc, G. (1834a). Extrait d'un Mémoire sur les Procédés Mécaniques et Chimiques pour Moyens de Reconnaître la Falsification de la Farine de Froment par la Fécula de Pommes de Terre. *Bull. Soc. Encourag., 354*. 441-444.
Dubuc, G. (1834b). Mémoire sur un Tabac à Priser Préparé des Feuilles de *Phytolacca Decandra* et Autres Végétaux Indigènes. *Précis Trav. Acad. Sci. Rouen*, 66-76.
Dubuc, G. (1837a). *Opuscules Scientifiques Concernant la Chimie, l'Histoire Naturelle, l'Industrie et l'Économie Rurale*. Brière, Rouen.

Frère, E. (1857). Dubuc (Guill.) in *Manuel du Bibliographie ou Dictionnaire Historique et Bibliographique*. Le Brument, Rouen.

Gaultier de Claubry, H. F. (1833). Rapport sur le Concours Relatif à un Procédé Propre à Reconnaître le Mélange de la Fécule avec la Farine de Blé. *Bull. Soc. Encourag., 354*. 441-444.

Kuhlmann, F. (1826-1827). Note sur le Phytolacca. *Rec. Trav. Soc. Sci., Lille,* 118-119.

Labat-Hacout, M. (1997). *Guillaume Dubuc, Pharmacien et Chercheur,* 1764-1837. Thèse d'Exercice: Pharmacie: Rouen.

Lemaire-Lisancourt, P. (1825). Note sur le Muriate de Chaux Employé comme Engrais. *Ann. Chim. Phys., 24*, 214-216.