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REVIEW BIBLIOGRAPHIC

NICOLAS DEYEUX

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ABSTRACT

Nicolas Deyeux (1745-1837), a French pharmacist, abandoned a prosperous professional practice to devote himself to research and academy. Among the many positions he occupied, the most special one was being the First Pharmacist of Napoleon. His most important researches (some with Parmentier), related to the composition of the milk of different mammals, the change experimented by blood during different illnesses, such as typhus and scurvy, the manufacture of beet sugar, the distillation of nutgalls, where he discovered gallic acid, indelible inks, ethyl nitrate, and mineral waters.

Keywords: digestion; gastric juice; physiology; sugar; urea.

RESUMEN

Nicolas Deyeux (1745-1837), un farmacéutico Francés, abandono una próspera práctica profesional para dedicarse a investigación y a la vida académica. Dentro de los muchos cargos que ejerció, el más especial fue ser el Primer Farmacéutico de Napoleón. Sus más importantes investigaciones (algunas con Parmentier) se relacionaron con la composición de la leche de diversos mamíferos, los cambios que sufre la sangre durante enfermedades como el tifus y el escorbuto, la fabricación del azúcar de betarraga, la destilación de las agallas, que lo llevó a descubrir el ácido gálico, las tintas indelebles, el nitrato de etilo, y las aguas minerales.

Palabras clave: azúcar; digestión; fisiología; jugo gástrico; urea.

INTRODUCTION

Life and career

Nicolas Deyeux (Figure 1) was born in Paris on March 21, 1745, the eldest of the three children of Didier Deyeux (?-1789) and Anne-Victoire Pia; the other two siblings were Claude-Didier (?-1794) and Adelaïde (?-1834). Nicolas took his basic education at the Collège Mazarin (one of the colleges of the University of Paris), and after graduation started immediately his apprenticeship at the pharmacy of his maternal uncle Philippe-Nicolas Pia (1721-1799), an establishment very popular among the rich people of Paris. After passing the examinations to become maître apothicaire (1772), he took over the business of his uncle and managed it very successfully for 15 years. In 1787, after amassing a substantial fortune, Deyeux sold the pharmacy to his uncle J. P. Boudet (who afterwards transferred it to his son Félix) and devoted all his energy to the study of chemistry in his private laboratory in the Rue de Tournon, together with his friend Antoine Augustin Parmentier (1737-1813). About the same time, Deyeux married Thérèse Denise Rosalie Moreau; their only son, Didier-

Théophile (1789-1849), became auditor of the State Council during the Empire period (Boudet, 1837; Chevallier, 1837; Dorveaux, 1921; Ramé, 1988).

The French Revolution brought tragedy to the family. Deyeux's brother, who was a Parisian notary, a royal supporter, was persecuted for his ideas, condemned, and guillotined on July 9, 1794. Nicolas was also bothered and became a suspect, but eventually was let go.

Deyeux passed away at Passy, on April 25, 1837, at the age of 93, and was buried in the Montparnasse cemetery. His wife, his son, and his sister Adélaïde survived him. The most important eulogies were pronounced by Etienne Pariset (1770-1847), the first permanent secretary of the Académie de Médecine; Moreau, professor of the Faculté de Médecine, Jean-Baptiste-Alphonse Chevallier, professor of the Ecole de Pharmacie de Paris; and Félix Boudet, successor of Déyeux at his pharmacy on Croix-Rouge (Boudet, 1837; Chevallier, 1837; Dorveaux, 1921; Ramé, 1988).

Deyeux lived a rich academic and public life. In 1774 he was appointed conseiller du Roi quartinier de la Vile for the Ile Notre Dame quarter (in charge of carrying on the ordinances of the city). At the time of the creation of the Collège de Pharmacie (1777), he was appointed to teach chemistry. From 1782 to 1797, together with Parmentier, he was one of the writers of Bibliothèque physico-économique, a journal on discoveries and improvements of the national and foreign industry, on the rural and domestic economy, on physics, chemistry, natural history, on domestic and veterinary medicine, and on sciences and arts relating to vital needs. At the beginning of 1795, Deyeux was appointed to the medical and pharmaceutical chair of the Ecole de Santé de Paris (which afterwards became the Ecole de Médecine, and then the Faculté de Médecine), a position he kept until 1822. In 1797 he was made member of the Institute of France in the chemistry section of the class of Physics and Mathematics. On July 6, 1802, Louis Nicolas Dubois (1758-1847), the first police prefect of Paris, made him a member of the Conseil de Salubrité et d'Hygiène in the Seine region, (administrator of civil hospitals). In 1803 he was elected, together with the anatomist François Chaussier (1746-1828), by the Ecole de Médecine to preside over the exams of the Ecole de Pharmacie and to inspect the offices of the department of the Seine. In 1804, Jean-Nicolas Corvisart (1755-1821), the First Physician of Napoleon, offered him to become the First Pharmacist of the Emperor Napoleon. As such, Deyeux dedicated himself to organize the pharmaceutical service of the imperial palace. Their work consisted in preparing all the medicines prescribed to the Emperor, his family, and afterwards, all of its employees. Deyeux kept this position until the first abdication of Napoleon (April 6, 1814). After Napoleon's return from the Ile of Elba, Louis-Claude Cadet de Gassicourt (1731-1799) was appointed to the position of First Pharmacist. In 1815 Napoleon appointed Deyeux chevalier of the Légion d'Honneur (Boudet, 1837; Chevallier, 1837; Dorveaux, 1921; Ramé, 1988).

During the Bourbon Restoration, Deyeux continued teaching his course of chemistry and pharmacy until the famous noisy opening session of the academic year of the Faculté de Médecine (November 18, 1822) where the students shouted against the abbé Dominique-Charles Nicole (1758-1835), which presided it as rector of the Académie de Paris, and others. This led to the abolishment of the Faculty and the dismissal of eleven professors, Deyeux among them (he was then 77 years old). Two years later, Louis XVIII created the Académie de Médecine and appointed Deyeux as titular member. On October 5, 1830, an order of Louis-Philippe reintegrated to their functions the eleven discharged professors, and Deyeux was called to fill the chair of pharmacy of the Faculté de Médecine. Deyeux was to old to occupy it and another person took over the chair (Boudet, 1837; Chevallier, 1837; Dorveaux, 1921; Ramé, 1988).

In 1790 a remarkable memoir about milk, written between 1787-1788 by Deyeux and Parmentier, earned them the prize that the Société Royale de Médecine de Paris had proposed for the best work on the physical and chemical properties of human and animal milk (Parmentier & Deyeux, 1790ab, 1799). In 1791 Deyeux and Parmentier won the prize again with their analysis of blood of sick persons, which was the title of the memoirs presented to the institution (Deyeux & Parmentier, 1791).

Besides of his two prize winnings essays, in collaboration with Parmentier, Deyeux carried on research on nutgalls and gallic acid (Deyeux, 1791), ethyl nitrate (Deyeux, 1797), discovery of oxalic acid in the hair that cover the pods of chick peas (Deyeux, 1798), plasters (Deyeux, 1799), cantharides (Deyeux, 1803), preparation of carbon monoxide (Deyeux, 1805), analysis of the sap of vine and hornbeam (Deyeux, 1806a), water distilled from inodorous plants (Deyeux, 1806c), mineral waters (Deyeux, 1808), indelible inks (Deyeux, 1810), production of by distillation of wood (Deyeux, 1815), and manufacture of beet sugar (Deyeux, 1810; Deyeux et al, 1800; Chaptal et al., 1800, Achard et al,, 1811).

Scientific contribution

Deyeux published about 25 papers on the different subjects he researched, as well as class notes for the courses he dictated. Here we discuss some of the most significant ones.

Gallic acid

One of the first publications of Deyeux was related to nutgalls and the analysis of gallic acid and the precipitate these two substances formed when treated with iron sulfate (Deyeux, 1791). In the first part of this memoir Deyeux mentioned that nutgall was the name given to an enlarged growth on an oak or other tree, produced by the puncture of an insect, for depositing its eggs. After describing the characteristics of the different varieties of this growth, Deyeux said that all these varieties had the remarkable property of precipitating aqueous solutions of iron salts. This property was attributed to the existence of an astringent principle, which many chemists had tried unsuccessfully to separate. The general belief was that this particular substance was an acid, named gallic acid, of yet unknown composition.

Deyeux decided to investigate this matter further, and for this purpose he treated the nutgalls with water, spirit of wine (alcohol), and ether, studied the action on alkalis upon the aqueous infusions, distilled the nutgalls as well as a mixture of them with water, and considered the different products he obtained (Deyeux, 1791).

Cold distilled water acted promptly on the nuts, producing, after 24 hours, a dark brown solution. Repeated extractions left in the flask a very small amount of solids, which were not affected by water or spirit of wine (aqueous alcohol). The same result (but faster) was obtained when boiling the nuts with water. The aqueous infusions decomposed rapidly when in contact with air; the surface of the liquid became covered with a pellicle that little by little settled on the bottom; nonetheless, the solution kept its property of producing an abundant precipitate when treated with iron sulfate. Carl Wilhelm Scheele (1742-1786) had already reported the formation of a surface pellicle on aqueous infusions of nutgalls and commented that although after its precipitation the solution was not longer astringent; it was still strongly acid (Scheele, 1786; Deyeux, 1791).

Deyeux filtered the aqueous infusion and then evaporated it to dryness over a water bath. The resulting solid was totally soluble in spirit of wine and ether; a small amount of it reacted with a solution of iron sulfate in the same manner as the infusion. When distilled in a glass retort, the residue first melted first and then released a large amount of CO_2, while a salt sublimed and deposited on the neck of the retort, as small fine needles. The final residue was amber colored acid liquor that effervesced with alkalis and deposited crystals of gallic acid. Examination of the sublimate proved that it was also gallic acid (Deyeux, 1791).

Treatment of an alcoholic solution of nutgalls with iron sulfate produced a strong blue solution and precipitate. Fixed alkalis and ammonia intensified their color and made it more transparent; non-caustic alkalis (Ca, Ba, etc.) produced an abundant white precipitate. Dissolution of the nutgalls was slower than with alcohol and yielded an amber colored liquid; treatment of the latter with water did not affect their transparency while treatment with iron sulfate turned it first blue followed by deposition of a black precipitate (Deyeux, 1791).

Deyeux found that gallic acid could also be prepared by distilling the nutgalls under vacuum, using a sand bath or naked fire to achieve a temperature above that of boiling water, in order to avoid deposit of the sublimated acid once formed. Initially a liquid passed over accompanied by CO_2. After 18 hours, the retort was separated from the fire and the remaining liquid found to be transparent, colorless, acid, having an undefined smell and flavor, and producing a black precipitate with a solution of iron sulfate. Left to evaporate spontaneously, it deposited needled crystals of pure gallic acid crossing each other in every direction. Afterwards reinitiating the distillation CO_2 was again produced abundantly while a solid salt sublimed in the neck of the retort in the form of small and extremely white needles. Subsequently, the sublimate disappeared being dissolved by a passing stream of oil (Deyeux, 1791).

The gallic acid obtained by this process was always colored and congested with oil, especially the one formed near the end of the distillation; for these reasons Deyeux purified it by sublimation. The purified acid reddened the blue vegetable tinctures and effervesced with alkalis; placed on burning charcoal, it inflamed and released an aromatic smell. Placed on a hot metallic plate, it melted, boiled, became black, and then carbonized. Distilled in a retort, it produced yellow acid liquor while some sublimed into the neck of the retort, and left behind a carbonaceous matter. Gallic acid was completely decomposed by repeated distillations; the decomposition was faster when distilling an aqueous solution of the acid. An aqueous solution of iron sulfate was the only one upon which gallic acid acted in a uniform way, always producing a fine shining black precipitate. The last section of the memoir was devoted to a description of the properties of this precipitate, which Deyeux, claimed was a combination of carbonated iron oxide and iron gallate (Deyeux, 1791).

Nitrate ether (ethyl nitrate)

In the eighteenth century the term ether was applied to all volatile liquids made by distilling mixtures of acids and alcohols. It was known as a general reaction and many types of ethers were prepared from the important acids (today we know that some of those ethers were actually esters or simple alkyl derivatives). It was believed that the acid was part of the composition of the ethers and thus the name they were assigned. All shared the common properties of being inflammable liquids with a characteristic smell. Louis-Jacques Thenard (1777-1857) had carried an extensive research on their preparation and properties (e.g. Thenard, 1807). The preparation of ethyl ether by the reaction of ethanol and sulfuric acid was a well-known process; many scientists had tried to prepare it using other acids such as nitric, hydrochloric, and acetic acid.

The combination of nitric acid with alcohol also yielded a product that chemists called nitric ether (today, ethyl nitrate) and several chemists had proposed modes for preparing it. Some believed that it was enough to mix the alcohol with nitric acid of medium concentration, and leave the solution in a cold place; after some days the ether was seen to float on the surface of the liquid. Others distilled a mixture of pure alcohol with smoking nitric acid and let the ether pass over. An additional procedure was to distill a mixture of alcohol, sulfuric acid, and potassium nitrate. It was well known that the color, savor, and volatility of this ether, depended strongly on the preparation method used. For example, the one prepared with smoking nitric acid, was usually very yellow and volatile, and released a brilliant nitrous vapor. The ether obtained from the distillation of a mixture of alcohol and sulfuric acid over potassium nitrate, was less yellow and volatile, and easier to keep than the previous one. Finally, the ether that separated spontaneously from a mixture of alcohol and nitric acid, contained a large amount of gas, which made its keeping very difficult (it even led to an explosion of the bottles). The ether prepared by all these methods tasted and smelled like nitric acid, although this characteristics vanished after some time; a heavy liquor was seen to settle little by little on the bottom of the container. The latter was found to be an aqueous solution of oxalic acid (Deyeux, 1797).

These characteristics led Deyeux to perform additional experiments to determine the identity of the coloring matter, the composition of the oily deposit, and the reason of the high volatility of nitric ether. As starting material he employed the ether prepared by the slow reaction of alcohol and nitric acid, known to lose most of its color spontaneously. He distilled four parts of nitric ether upon one part of sugar in powder and noticed that the operation went on gently, with almost no disengagement of air; the residual liquor was very aromatic and much less colored. A second distillation over fresh sugar whitened the ether still more; but decreased its amount; further similar distillations resulted in an almost total decomposition of the ether. The process was easily carried on at the temperature of boiling water. The final residue was a slightly inflammable liquid, without the smell, taste, and volatility of an ethereal fluid, accompanied by melted sugar of yellow color. The surface the latter was covered by a very combustible oil of the same color, having a sharp taste and penetrating smell, soluble in oils, alcohol, and sulfuric ether (diethyl ether), and forming soap with potassium and ammonia. Deyeux believed that this oil was analogous to the one obtained during the latter stages of the distillation of sulfuric ether, and known as *sweet oil of vitriol*. Deyeux concluded that this oil was the source of the yellow color of nitric ether (Deyeux, 1797).

Deyeux also thought that nitric ether owed its volatility to the nitrous gas (NO_2), which continually escaped from it. To determine the presence of this gas he mixed sixteen parts of water with one of nitric ether and put the solution into a bottle furnished with a curved tube plunging under a bell-glass filled with water. The bubbles that disengaged displaced the water under the jar, and allowed measuring the volume of the gas released. This gas was first washed several times to separate any impurities it might contain, and then one portion of it was mixed with atmospheric air, and another portion mixed with oxygen. In both cases Deyeux noted the formation of a vapor red as the one liberated by the most concentrated nitrous acid. A lighted candle plunged into this gas, produced a flame similar to that of the combustion nitric ether (Deyeux, 1797).

Deyeux concluded that the high volatility of nitric ether was not due to its nature but by the separation of this gas, which always carried with it a certain quantity of nitric ether. He attributed the presence of nitrous gas to the extreme facility with which the nitric acid was decomposed, without believing that it was essential to the constitution or formation of nitric ether, since, when deprived of it, this ether kept like other ethers, without breaking the vessels that contained it (Deyeux, 1797).

Milk

One of the first paper published by Deyeux at the beginning of his academic career (he was already a demonstrator at the Collège de Pharmacie) was a comparison of the milk of two cows fed successively by ordinary fodder and then by corn stalks and leaves (Deyeux, 1793). This project was carried on to find an alternative food to common fodder when the weather inclemency affected its supply. Parmentier had already proved that feeding stalks and leaves of corn did not affect the health of the cattle (Parmentier, 1784).

Deyeux fed the cows for ten consecutive days first with ordinary fodder and then with corn stalks and leaves; milked them every day and examined the milk, raw and boiled, its cream, the franchipanne (the solid residue left after evaporating the skimmed milk), and its serum. The results indicated that the milk produced by the cows fed a corn diet was sweeter and more fluid than that produced by cows fed ordinary forage. In addition, it did not have the same odor, contained less cream (the cream was almost tasteless), contained less franchipanne, and less milk salt (lactate). The difference in odor and sweetness was easily understood from the known fact that the odor of the cream and the taste of the milk were strongly affected by the odor and taste of the vegetables that composed the forage (Deyeux, 1793).

The Société Royale de Médicine offered a prize for the best memory reporting a comparative examination of the physical and chemical properties, as well as the nature, of the milk of a woman, cow, goat, ass, ewe, and mare. On February 23, 1790, the first prize was assigned to the comprehensive work (111 pages) presented by Parmentier and Deyeux (Parmentier & Deyeux, 1790ab, 1799).

In the first stage of their work, Parmentier and Deyeux decided to analyze one of these milks (cow) in full detail and use the results to compare it with milks of other sources. The two scientists worked more than a year testing milk in different states: crude, boiled, diluted in water, fermented, and coagulated. They used cows of the same age and subjected them to a different feed regimes based on wilted potatoes, corn stalks, sorrel, artichokes, onions, red beets, etc. They also studied butter and cheeses. The particular odor of cow milk could be easily separated by distillation over a water bath; the distillate did not held for a long time, in less than 15 days it became turbid and acquired a putrid smell. All the animal milks tested showed this behavior. Milk itself, left alone in a cold place, became covered by an unctuous yellow liquor having a sweet and agreeable taste; this cream, agitated strongly, produced the butter. Butter changed in flavor, color, and consistency according to the season and the feed; dry forages produced a darker butter, green feeds generated a yellow butter. Skimmed milk, left alone, turned sour and yielded a gelatinous white substance, called caseinous matter, which floated on the serum. Both phases could be easily separated by decantation. The milk could also be curdled by addition of alcoholic liquors, gum Arabic, sugar, acids, sulfates, artichokes, etc. Parmentier and Deyeux discussed their experimental results on the: (a) physical and chemical characteristics of milk: properties, volatile and non volatile fractions, cream components, casein material, salts in serum, and fermentation; (b) medical aspects: influence of food, medicines, mood, and physical feelings, milk and its components as medicines, and milks of different origin, and (c) agricultural economy aspects: dairy, production of butter, cheeses, industrial uses of milk including manufacture of milk alcohol and vinegar (Parmentier & Deyeux, 1790ab, 1799)

Some particular results were as follows: The cows selected were of the same age and strength and were fed in the same stable, and, within possibility, under the most similar conditions, except for their food. Some cows were fed with the leaves of corn, others with cabbage, some with small potatoes, and some with common grass. The milk of the former was very sweet; that of the second was the least agreeable to the taste, and that of the third and fourth, was the most serous and insipid. Similar comparisons were also made of the odor and the characteristics of the distillation fractions. Parmentier and Deyeux concluded that the volatile substance which conferred milk its particular odor, was a constituent part of it, and hence, not destitute of utility, and that for this reason it was not advisable (!) to boil the milk employed for food or diet. In the case of cream, the influence of the diet manifested itself either by letting the creams stand until a green efflorescence was formed of a cheesy nature, and which, with the addition of salt, could be eaten as cheese; or after being agitated during half an hour. For cows fed with corn, the resulting semi butter was insipid, very firm, and of a light color; from cows fed with potatoes, it was equally insipid, of similar color, but softer and greasier, cabbage gave a strong taste, common pasturage yielded the most delicate cream, both in flavor and color (Parmentier & Deyeux, 1790ab, 1799)

Parmentier and Deyeux carried several experiments to determine whether butter was a component of cream that was simply separated by agitation or churning, or was the result of a chemical process that occurred during these operations. They believed that the latter explanation was the correct one because it was not possible to separate the particles of butter in any other manner. Cream, left in the milk, yielded fat cheese, but not butter (Parmentier & Deyeux, 1790ab, 1799)

The rancidity of butter originated entirely from the mass coagulated, or cheesy matter, which was mixed with it. The remaining fluid, the whey, was incapable of coagulation.

In the second stage of their work, Parmentier and Deyeux proceed to analyze milk of other sources. Their first experiments were made on milk taken from a woman four months after giving birth. They observed that after the cream had risen, the lower part appeared of a more perfect white and did not coagulate with vinegar or diluted mineral acids. They attributed this result to a superabundance of serum. Further experiments showed that the quantity of cheesy substance increased according the age of the milk, and that it became easier to coagulate by acids. The cream could not be changed into butter; instead it formed a viscous soapy substance. Ewe's milk resembled woman's milk in its color, taste, and consistence, but a chemical analysis showed the following peculiarities: The odor of the distilled vapor was almost imperceptible; and although it did not appear to contain anything in solution, yet it deposited a sediment similar to the lymph of cow's milk. Although all acids coagulated this milk, the coagulum was not uniform but formed distinct floccules. The cream was not abundant and was changed with difficulty, into a soft butter, which rancid promptly.

The cream of goat's milk was thick and had an agreeable taste. In contact with air, goat's milk could be preserved longer than any other species, and the skim on its surface would slowly be change into a tasty cheese. Goat's butter was firm, formed easily, and did not become rancid.

Sheep's milk was very similar to that of a cow. Its cream easily separated by standing; it was yellow, of an agreeable flavor, and provided a large amount of butter, which unfortunately, became rancid very rapidly (Parmentier & Deyeux, 1790ab, 1799)

Blood

In 1794, the Société Royale de Médicine offered a prize for the best memory reporting the changes that took place in blood during different types of illnesses, including scurvy. Once again, the first prize was assigned to the comprehensive work (56 pages) presented by Parmentier and Deyeux (Parmentier & Deyeux, 1791, 1794).

Parmentier and Deyeux's assay was divided into three main chapters (Deyeux & Parmentier, 1791, 1794). The first one gave a historical review of the chemical information available about blood, the second was a description of the different experiments and measurements they performed in order to familiarize themselves with the action and different principles of blood, and the third, an examination of the blood of subjects affected by inflammatory and putrid febrile sicknesses, and scurvy.

In the first part of their report, Parmentier and Deyeux made an historical review of the results obtained by scientists such as Leuwenhok, Hales, Rouelle, Hewson, Menghini, Bucquet, and Fourcroy. Hales had measured the gases released during the distillation of blood, Menghini had shown that it contained iron, and Rouelle Jr, had determined a reasonable analysis of blood. At the moment that blood of a live animal left the vessels, it differed very little with respect to its physical composition and behavior, but when it was allowed to rest, it soon lost its fluidity, temperature, odor, and homogeneity, and coagulated into a solid mass of the consistence of curdled milk. This mass gradually separated into a yellow fluid (the serum) and the coagulum, which retained the red color. The proportion between both parts varied much in different animals, and even in the same animal depending on the circumstances (Parmentier & Deyeux, 1791, 1794).

After carrying on numerous experiments, Parmentier and Deyeux concluded that blood was composed of nine principal parts: the odorous part, the fibrous substance, albumen, sulfur, gelatin, the red part, alkali or soda, and water. The neutral salts, which were generally found in blood, seemed to be foreign to it as it was certain that blood could exist without them, and that their presence was due to particular circumstances. The relative proportion of the different components varied largely, according to the age, the temperament, and way of life of the person (Parmentier & Deyeux, 1791, 1794).

The odorous part in a healthy subject was very obvious, particularly in fresh blood. It gradually grew weaker as the blood changed and disappeared completely once putrefaction took place. In the blood of a sick person, the odorous part was decidedly less observable. Its affinity to the serum appeared to be less than to the coagulum. According to Parmentier and Deyeux, there was a clear analogy between the odorous part of the blood and that of vegetables because both, independently of their action on the odorant organ, were “soluble in air”, in water, and in alcoholic liquors. The fibrous substance appeared to exist in solution or in a state of high division. Any quick motion given to the blood as it issued from the vessels was sufficient to cause its separation. Diluting the blood in water could also separate it. In the first case the fibrous matter appeared as a mass of attached filaments, while in the second it consisted of membranous pellicles. The fibrous substance undoubtedly contributed to the formation of the coagulum. The red part appeared in a large variety of shades; that of young people was red-rose, that of older people was darker; the red color of venous blood was weaker than that of arterial blood. Parmentier and Deyeux reported that in spite of the many experiments done, they had been unable to separate the coloring matter. Nevertheless, they believed that iron was the principal matter connected with coloring the blood and that its solution in the blood was carried out by means of a fixed alkali analogous to soda. They were surprised that only the red part of blood contained iron and that the muscular substance, which they believed was completely produced by the blood, did not contain the element, even in minute amounts. In blood that remained unaltered, the albumen was always dissolved in the serum, but at soon as blood decomposed, it separated into two parts. The albumen of blood was very similar with that of the white of an egg and other animal fluids; they had the same properties and all contained sulfur. Of all the constituents of blood, albumen was the only one that became altered in sick persons. Alkali always accompanied blood in considerable proportion. It seemed that one of its principal roles was to promote the solution of bodies (e.g. iron and albumen) that otherwise would remain insoluble. It was difficult to give a definite explanation for its origin, but it seemed probably that it came from the digestion process. Many famous physiologists had argued the possible presence of gelatin in blood, probably because its amount was so minute that made the analysis very difficult. Anyhow, this small quantity did not seem to be affected by the state of disease. The fluidity of blood depended essentially on the amount of water it contained, which was not always the same, independently of the health of the subject examined (Parmentier & Deyeux, 1791, 1794).

Parmentier and Deyeux also examined the blood of persons laboring under different diseases. Blood drawn from people working under inflammation rapidly became covered by a white crust (the buffy coat), which they found consisted of fibrin. The underlying material was softer than usual and almost completely soluble in water. The albumen of did not coagulate as usual when heated, but became milky when mixed with water. The blood of patients affected with a putrid fever (typhus) did not present a constant behavior; sometimes it showed the buffy coat and sometimes it was similar to that of healthy persons. The blood of scurvy patients was similar to that of healthy people, except for a peculiar smell and not coagulating easily. The serum of diabetes patients frequently had the appearance of whey, but did not contain sugar, although the urine was loaded with it (Parmentier & Deyeux, 1791, 1794).

Parmentier and Deyeux examined repeatedly blood drawn from patients suffering fevers of the worst form. It did not yield volatile alkali by distillation, and did it become putrid sooner than blood from the healthier person. However, in various diseases, the albumen seemed affected; its union with the serum was less complete and its solidity less perfect than in health. By analysis, the buff, when present, was similar to that from inflammatory diseases, and the under laying coagulum was tender: it was soluble in water and the solution was coagulated by heat, alcohol, and concentrated acids, while fixed and volatile alkalis rendered its color more vivid, and prevented the coagulation (Parmentier & Deyeux, 1791, 1794; Deyeux, 1806b).

Inks

Deyeux was the reporter of two committees appointed by the Académie des Sciences to comment on problems related to indelible inks. The first committee was constituted by Claude-Louis Berthollet (1748-1822), Louis Nicolas Vauquelin (1763-1829), and Deyeux, and instructed by the chemistry class to give an account of the memoir of Dr. B. H. Tarry related to the methods employed for removing writing from paper, the processes for restoring writing, which had been apparently destroyed, the best ways for improving common inks, and the discovery of an ink, which resisted all chemical agents (Berthollet, et al., 1810).

The art of erasing writing was very ancient, and the means employed were very simple: It was enough to moisten a written paper with any acid to cause the writing to gradually disappear. All acids could not be used with equal success; some left a hard to remove stain on the paper and others corroded the paper and rendered it unsuitable for future use. The way to avoid these hassles was to use an acid, which acted only on the writing, without injuring the paper, or giving it a color different from the original one. In order to discover which acids were best suited for this purpose, Tarry submitted common writing inks to the action of different acids and carefully observed the phenomena, which resulted from their action. Sulfuric acid easily destroyed the writing but at the same time it gave the paper an oily tint. Potassium acid oxalate produced quicker and clear effects. Fresh chlorine seemed to be preferable to the above two acids because it destroyed the writing and simultaneously bleached the paper without altering it. This was not the case with nitric acid; it always destroyed the writing but penetrated the paper and formed upon it undulating yellow lines.

These two limitations could be partly remedied by diluting the acid with enough water, or by washing the paper as soon as the writing had disappeared. A mixture of nitric and of hydrochloric acids acted slowly upon writing. It bleached the paper and did not resist its drying, as when employing the nitric acid alone. In general, whatever acid was used, it was appropriate to immerse the paper in water, in order to dissolve the new combinations, which the acids had formed with the ink particles that had been eliminated (Berthollet et al., 1810).

At the end of his paper, Tarry mentioned that China ink did not behave with acids like common ink, as its composition was very different. Instead of destroying the writing, acids that attacked China ink changed its color to a deep black, which could only be destroyed by a scraper.

As seen above, all the methods used for destroying writing were based on decomposing the ink and forcing its constituent parts to form new combinations. These combinations, after being decomposed in their turn by different agents, could recover a color, which, if not that of original ink, at least exhibited a shade sufficiently evident for recognizing the letters and words that had been traced on the paper before it was touched by the acids. According to Tarry, gallic acid was one of these agents, which in this case did very well. Other appropriate agents were a solution of calcium prussiate or of the alkaline hydrosulfides. Unfortunately these agents never succeeded if the acids had been left in long contact with the writing, and if the paper had been washed afterwards. It was easily visualized that in this case the constituent parts of the ink, which had combined with the acid and formed with it combinations soluble in water, by being washed away by the water they would not to leave any traces of their existence, and consequently, recovery agents, such as calcium prussiate, were unable to render them visible (Berthollet, et al., 1810).

Most of commercial inks were known to be of poor quality. Some were spontaneously destroyed; others gradually lost their black color and became yellow; some, after some time, penetrated the paper and spoiled it, and finally, others become darker with time. All these effects originated from the nature of the substances employed in the making of the ink. Convinced of the advantage of having good ink, Tarry, after carrying on a series of experiments to obtain an ink of superior quality, was forced to admit that he had not discovered any recipe superior to that published by Lewis. Lewis's ink combined every advantage but, at the same time, it was no more exempted than the rest from being dissolved by acids, and in this respect it had an inconvenience, which those who wished to erase writing, knew very well how to profit by (Berthollet et al., 1810).

For this reason, Tarry made new experiments in order to obtain ink unalterable by chemical agents, and saw his efforts crowned. According to Tarry, his ink was composed on principles different from those of common inks. It did not contain gallnuts, Brazil wood or logwood, gum, or any preparation of iron; it was strictly vegetable, it resisted the action of the strongest acids, of the most concentrated alkaline solutions, and of all solvents. Nitric acid had little effect on the writing performed with this ink. Chlorine changed its color to that of pigeon's dung; after this action, caustic alkaline solutions changed it to the color of iron carbide, although the characters of the writing persisted unaltered. The principles of which it was composed rendered it incorruptible and that it would retain its properties many years (Berthollet et al., 1810).

According to Deyeux, the results of the tests carried on by the committee verified Tarry's claims and showed that his ink was the best they had ever seen, within the category of indelible inks. Nevertheless, it had a defect common to all indelible inks: it was liable of depositing quickly sediment in the bottles and inkstands, which deprived the liquor above it of the qualities it had before. This fault disappeared easily if the bottle was shaken at the time the ink was used (Berthollet et al., 1810).

During the early part of the nineteenth century France was facing an increasing number of disorders caused by unscrupulous people who were buying old legal papers at a cheap price, changing their contents, or erasing them completely, and selling them at a lower price than new fiscal stamped papers. For this reason, Marthe Camille Bachasson (1801–1880), the Minister of the Interior, approached the Académie des Sciences and requested recommendations for solving the problem. The Académie understood the gravity of the problem and appointed a committee consisting of Joseph-Louis Gay-Lussac (1778-1850), Pierre-Louis Dulong (1785-1838), Jean Chaptal (1756-1832), Deyeux, Louis-Jacques Thenard (1777-1857), Jean d'Arcet (1725-1801), Michel Eugène Chevreul (1786-1889), and Georges Simon Serullas (1774-1832) to provide the Minister with an adequate answer. On the 6th of June 1831, d'Arcet reported their findings to the Académie (d'Arcet et al., 1831).

The committee considered two alternatives: (a) use of a totally indelible ink to be applied to ordinary paper, or (b) use of a paper prepared in such a way that it was impossible to change writing done with common ink, without leaving traces of its falsification (safety paper). After examining the many indelible inks and papers available, including new ones proposed to the committee, the committee found that the falsification of written documents could be fully prevented using ink prepared by one of the following procedures: (a) Indian ink (or in its absence, the imitation of it made in Europe, with soot, and animal glue, or gum) dissolved in a an aqueous solution of HCl of specific gravity 1.010; or (b) Indian ink dissolved in a mixture of aqueous manganese acetate of 1.074 specific gravity, and half its weight of an aqueous solution of pure sodium carbonate. These inks became perfectly indelible when exposed to the action of the vapor of aqueous ammonia. Anyhow, the committee remarked that no ink, kept in a liquid state, could be indelible, as the coloring matter, from its excess of density, would eventually settle down (d'Arcet et al., 1831).

Regarding the paper, the committee recommended that it be printed using cylinders, not plates, and carrying specific marks that should be located to the right of the stamps, on the center, and along the length of each page. These marks should be printed with a color based on the black precipitate that deposited in the furnaces used by hat makers, or dispersed in the paper paste. In addition, legal paper should carry a legal date, imprinted in the paste or on the stamps (d'Arcet et al., 1831).

Beet sugar

In 1799 M. A. N. Scherer sent a letter to Jean-Baptiste Van Mons (1765-1842) (Scherer, 1799) informing him that Franz Karl Achard (1753-1821) had found a replacement of sugar in the roots of beet, a plant which had so far almost entirely used as animal food. Another letter to Van Mons by Achard himself followed the one by Scherer (Achard, 1800). Achard took 25 beet roots in their rough state, weighing 32.5 lb, eliminated the skin, head, and roots, cut the reminder into very small pieces, and then pressed it to extract their juice. The residual paste was again extracted by means of hot water; the two extracts, weighing 14.75 lb, were united, strained through a flannel, and then evaporated by slightly boiling in a tin vessel, until it reached the consistence of honey. During this evaporation, the accompanying impurities spontaneously separated and were carried away by the coagulation of the albumen of the roots. The thickened juice was further evaporated until it became a rather thick mixture of a crystalline substance and a fluid but viscous matter, which were separated by press filtering through a bag. The sugar, after drying, yielded a yellow muscovado (a unrefined sugar, with a strong molasses flavor) composed of regular crystals, having very good taste, and being perfectly sweet. A sugar of any quality may be obtained by refining this muscovado. Achard remarked that the all the waste parts arising from the process could be used to prepare fine alcoholic liquor. According to Scherer, from 32.5 pounds of roots it was possible to obtain 3.20 pounds of raw sugar. Additional tests led Achard to estimate that 100 lb of beet roots yielded 8 pounds of the purest refined sugar, that is, 180 square yards of land, which could produce 46,000 pounds of roots, ought to yield twenty-two quintals of raw sugar (Scherer 1799, Achard, 1800).

Achard also reported that the *beta vulgaris* Linn. variety was the proper one for making of sugar, and estimated that could manufacture sugar at a little less than 2-3/4 pennies per pound.

Achard's letter produced a great sensation in France; it was reprinted in every newspaper, and led the Institute of France to send Deyeux to Germany and make a report upon Achard's process. The significance of Achard's process was further analyzed and investigated by a committee appointed by the Institute. The report of the committee (Deyeux, et al., 1800) was divided into three sections. The first part one dealt with the experiments that had been conducted in order to determine the exact amount of sugar contained in the sugar beet cultivated in France, the second part was an analysis of Achard's process, and the third part described the experiments done in order to improve Achard's method.

In order to ascertain the amount of sugar in the beet, the root was cut into small pieces and digested for some time with alcohol. Evaporation of the alcoholic solution produced a crystallized mass accompanied by a substance like molasses. Although the proportion of sugar was substantial (2/32 of the raw weight of roots, that is, 6.25%), the committee understood that the amount of alcohol required was inappropriate for an economical operation. They repeated Achard's process (water extraction) and obtained a quantity of good sugar, but in lesser amount than that obtained by an alcohol extraction. They also found that refining the sugar led to a loss of 1/6 more that the sugar from cane. Achard's method was able to produce a true muscovado. The pure sugar it yielded was very similar to the one obtained from sugar cane, but during the process part of the sugar was decomposed and could not be crystallized. Many experiments were done, without success (using limewater, ox blood, egg white, a solution of cinders, etc.), trying to separate from the juice a mucous substance, which seemed to be mixed with it and to prevent its crystallization. Their only suggestion was that the root should not be boiled but should be grated down into a kind of pulp, followed by strong pressing. Boiling the roots decreased the yield, probably because part of the sugar combined with other substances present in the roots (Deyeux, et al., 1800).

The committee made some rough economical calculations and concluded that 3,419 square meters of land should produce about 25,000 kg of beetroot, that the costs associated with the cultivation represented about 250 francs, while the expenses associated with the extraction of the sugar amounted to about 150 francs. The raw roots would produce 391 kg of muscovado and these would yield 224 kg of pure sugar. Considering the labor costs, it was possible to estimate a final cost of 90 centimes per half-a kilo of sugar (without taking into account the possible benefits from the residual matter) (Deyeux, et al., 1800).

The results of the war between England and France, as well as the embargo on British goods decreed by Napoleon, with the corresponding increase in price of imported sugar, led to further work by Deyeux (Deyeux, 1811). In his new memoir, he gave again a detailed description of Achard's process, now mentioning that the fresh juice extracted was treated with sulfuric acid, then left alone for a few hours to allow precipitation of the solids, followed by addition of limewater or quicklime to precipitate the unreacted acid. According to Deyeux, his new experiments proved that the addition of sulfuric acid did not have the favorable effect claimed by Achard; it was actually detrimental because in addition to coagulating the albumen (a positive effect), it acted over the immediate materials present in the juice and provoked an alteration of the sweet molecules and made them difficult to be separated. Instead of producing clear syrup, it generated a very thick and viscous magma that did not allow the formation of crystals. It was impossible to add the required amount of limewater to neutralize the acid; the excess material remained in suspension and formed with the sugar molecules a combination very difficult to break down. Not only that, it also communicated a disagreeable taste to the final sugar (Deyeux, 1811).

For these reasons, Deyeux believed that the best procedure to follow was the one the commission had suggested succinctly in its report (Deyeux, et al., 1800): Here the beet roots were washed in a tub, then grated by the hand with an instrument exactly like a kitchen grater, and finally squeezed in a wooden screw-press. The juice was then boiled into a syrup (some persons adding a little chalk or lime to it, to separate feculences), and when it had attained a certain degree of concentration, it was boiled with ox blood, strained, boiled down once more, and then put into a warm room upon flat trays where, if the process was well conducted, a portion of it crystallized out in the course of about eight hours. Afterwards the syrup was drained off and the crystals drained put upon linen cloths. The separated crystals had a strong brown color and a very disagreeable taste, and hence had to be purified. After many experiments, Deyeux found that the best way to purify the crystals was to pour on them a little water and then press the wet mass (Deyeux, 1811).

Napoleon ordered that the recommendations of Deyeux should be part of booklet giving instructions about the cultivation of sugar beet and the extraction of its sugar (Achard et al., 1811).

The reader interested in the fascinating story of the efforts done during the Napoleonic government to replace cane sugar by sugar produced from raisins and sugar beet, is referred to the papers by Fournier (Fournier, 1997, 1999) and McMurtrie (McMurtrie, 1880).

Fig. 1: Nicolas Deyeux (1745-1837)

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