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Pierre-Jean Robiquet

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ABSTRACT
Pierre-Jean Robiquet (1780-1840), a French pharmacist, made important contributions in the areas of mineral chemistry, mineral and vegetable pigments, and extractive and analytical chemistry. Alone, or with his collaborators he discovered asparagine (with Vauquelin), alizarin and purpurin in madder (with Colin), orcin, and orcein in lichens, glycyrrhizin in licorice, cantharidin in cantharides, amygdaline in bitter almonds (with Boutron-Charlard), caffeine (independently of Pelletier, Caventou, Runge) and narcotine and codeine in opium.

KEYWORDS: vegetable dyes, alizarin, purpurin, orcin, glycyrrhizin, cantharidin, amygdalin, alkaloids, caffeine, opium, morphine, codeine

Resumen
Pierre-Jean Robiquet (1780-1840), farmacéutico Francés, realizó importantes contribuciones en las áreas de química mineral, pigmentos minerales y orgánicos, y química extractiva y analítica. Solo, o con sus colaboradores, descubrió la asparagina (con Vauquelin), la alizarina y la purpurina (con Colin), la orcina y la orceína en líquenes, la glicirrizina en regaliz, la cantaridina en las cantáridas, la amigdalina en las almendras amargas (con Boutron-Charlard), la cafeína (independientemente de Pelletier, Caventou y Runge), y la narcotina y la codeína en el opio.

Life and career (Bussy, 1841; Dains, 1936; Maurice, 1992; Warolin, 1999)

Pierre-Jean Robiquet was born in Rennes, France, on January 13, 1780; one of the four children of Jean-François Robiquet, a printer and bookseller, and Marguerite-Jeanne Miché. He begun his studies at the free school of Château-Gontier but when he was in his fifth grade the institution was closed down because the teaching priests refused to take the fidelity oath demanded from all clerics by the *Constitution Civile du Clergé* (Civil Constitution of the Clergy) of 1791, which replaced the Concordat of 1516 and subordinated the Roman Catholic Church in France to the government. Consequently, his father decided to orient his son towards the career of architecture. Thus he began new studies, leading him to master the arts of design, perspective, woodsman, and carpentry. Once again the results of the Revolution affected his future and seriously disrupted his infancy. His father was the official printer of the departments of d'Ille and Vilaine and as such was assumed to have taken part on the elaboration of the decrees that led to the arrests of the Girondin deputies that provoked the insurrectional movements of May 31-June 2, 1793. He and his wife were arrested, their property confiscated, and their business ruined. Friends of this father took their four children, suddenly left without lodging and resources, into their care. By lack of alternative, Robiquet entered as an apprentice to a carpenter, who for a certain payment and conditions, agreed to teach him the art. To take him out of this painful situation, it was decided to put him under the tuition of a good relative living in Lorient, and who, after a year, succeeding in getting him an apprenticeship in the pharmacy of Clary (Bussy, 1841). Robiquet stayed in this position for one year (1794-1795) and then moved to the more important pharmacy of the Navy, managed by L. Chedeville. After his father was released from prison, he decided to return to his family in Rennes. He now took advantage that public schools had been opened to attend the courses at the École Centrale and complete his classical studies. At the same time, he found a position at the general pharmacy of the Army of the West. Afterwards his father sent him to Paris to complete his pharmaceutical education. His employer recommended him to attend the course given by Antoine-François Fourcroy (1750-1809) at that institution. This was a turning point in Robiquet's life; he was then 16 years old and became so fascinated by the ability of the eloquent professor that decided to make chemistry his profession (Bussy, 1841). Robiquet's father helped him to get a resident position at the laboratory that Fourcroy owned together with Louis Nicolas Vauquelin (1763-1829) for the fabrication of chemical products. There he took part in their research about urinary calculi (Warolin, 1999).

In 1799 Robiquet was inducted into the army and during 1799 and 1801 participated in the campaigns of Italy as military pharmacist of third class. He used this period to attend the university of Pavia, where listened the lectures of Alessandro Volta (1745-1827) on physics and of Antonio Scarpa (1752-1832) on anatomy. After the French victory at Marengo he was appointed pharmacist at the teaching hospital in Rennes (1801); he stayed in this position until 1804, when he transferred to the hospital of Val-de-Grâce. This last position filled in one of his most intense desires, because it

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brought him to Paris, the center of sciences. In 1807 he abandoned the military career to fully dedicate to chemistry, and entered the chemical factory that Vauquelin and Fourcroy had in the Colombier street. His first works about asparagus, which led to the discovery of asparagine, and about the cantharides (Spanish fly) date from this period.

While studying pharmacy Pierre-Jean married Laurence-Jacquemine Robiquet (1787-?), his first cousin, in 1807. They had three children, Sophie-Eugénie, Laurence-Adelaïde, and Henri-Edmond (1822-1860). Shortly (1808) thereafter he graduated as pharmacist. In order to support his home he quit his job at the chemical factory and bought a pharmacy. In 1811 Robiquet was appointed *répétiteur* at the École Polytechnique, replacing Jean-Antoine Cluzel (-1813), and in the same year, after the death of Jean Nicolas Trusson, he was also appointed adjunct professor at the École de Pharmacie of Paris. After the sudden death of Jacques-Paul Vallée (1811) Robiquet replaced him at the chair of natural history of medicines of vegetable origin, with Joseph Pelletier (1788-1842) as his adjunct. Robiquet was just 26 years old (Warolin, 1999).

In 1826 he associated with Aristide Boyveau, and then with Pierre Joseph Pelletier (1788-1842), to exploit a chemical industry in Issy, manufacturing chemicals and quinine sulfate. In 1830 Robiquet hired a young pharmacist, J.-B Berthemot and put him in charge of the operations for extracting opium, a task which led to the isolation of codeine (Warolin, 1999).

His delicate health forced Robiquet to resign his academic activities and accept (1824) the position of administrator-treasurer of the École de Pharmacie, a position he held until his death. He was a founder (1824) and first president of a society for promoting the welfare of the pharmacists of Paris and the department of the Seine, and defending their professional interests. He was elected to the Société de Pharmacie in 1809, where he occupied the functions of general secretary for 21 years (1817 to 1824 and 1828 to 1840). In 1826 he was elected President of the Société. He was elected to the Académie Royale de Médecine in 1820 and became secretary of the pharmacy section between 1822-1824. In 1833 was admitted to the Académie de Sciences, replacing Jean-Antoine Chaptal (1756-1832) in the chemical section. He was elected to the Légion d'Honneur (Warolin, 1999).

In the latter part of his life, Robiquet was in ill health, suffering from gastric trouble and nervousness. In April 1840 he suffered an attack of cerebral paralysis and after a few days of intense suffering he passed away in Paris on April 29, 1840. He was buried in the Montparnasse cemetery; unfortunately his tomb was abandoned and the remains transferred to the bone yard of Père Lachaise on February 5, 1973 (Warolin, 1999).

His main activities were in the areas of mineral chemistry, mineral and vegetable pigments and extractive and analytical chemistry. In inorganic chemistry he studied the preparation of pure baryta, the spontaneous decomposition of barium bisulfate, purification of nickel by means of hydrogen sulfide, the action of aqua regia on antimony, purification of borax, boric acid, the use of KCN in medicine, preparation of Prussian blue, etc. etc. (Warolin, 1999). His research on vegetable dyes and active principles included the analysis of asparagus juice and isolation of asparagine (with Vauquelin), isolation of alizarin and purpurin in madder (with Colin), of orcin, and orcein in lichens, the discovery of glycyrrhizin in licorice, analysis of cantharides and discovery of cantharidin, discovery of amygdaline in bitter almonds (with Boutron-Charlard), discovery of caffeine, independently of Pelletier, Caventou, and Runge, and the discovery of narcotine and codeine in opium, etc. etc.

Scientific contribution

Robiquet published some 60 papers in the period 1805-1835, in the areas of mineral chemistry, mineral and vegetable pigments, and extractive and analytical chemistry. As customary for a candidate to the Académie des Sciences, he published a booklet detailing his main research achievements.

Vegetable dyes

Madder lake is a traditional lake pigment, extracted from the roots of common madder plant (*Rubia tinctorium*), which had long been prepared by cloth dyers by simply washing the roots with water. Several scientists had investigated the dyeing characteristics of madder but except for Charles Frédéric Kuhlmann (1803-1881) (Kuhlmann, 1823), none had tried to separate the dyeing principle in a pure form. According to Kuhlmann the root contained a red and a brown coloring matters, malic acid, mucilage, gum, sugar, a bitter substance, a fragrant material, woody matter, and inorganic salts. In 1826 Robiquet and Colin repeated Kuhlmann's work, using a different extraction procedure (Robiquet and Colin, 1826). They had already noticed that macerating the roots with 3 or 4 parts of water during only 8 to 10 minutes produced a red-brown acid liquor that gelled after a time, which depended on its concentration. The solution was completely soluble in alkali. The resulting liquid provided lakes with a dirty color, indicating that it was highly contaminated. In order to purify it, the jelly material was filtered, washed with a little water and then with alcohol, and then distilled to remove the alcohol. Additional washes with water, treatment with diluted sulfuric acid, followed by gentle heating, allowed them to separate the coloring principle, which they named *alizarin*, derived from the expression *alizari* used in commerce to designate the full root of madder.

The changes in color observed during the different purification stages led Robiquet and Colin to suspect the presence of a second coloring matter in the roots of madder. Eventually they separated it and named *purpurin* because of its red purple color (Robiquet and Colin, 1827). Purpurin crystallized in the form of needles, which were less soluble