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BIBLIOGRAPHIC REVIEW

JULES-MARIE-AUGUSTIN CHAUTARD

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ABSTRACT

Jules-Marie-Augustin Chautard (1826-1901), a French multifaceted scientist who started as a pharmacist and then turned physicist and coin collector. His main activities were related to phenomenon of light polarization, particularly in camphor and lavender, and the spectral study of chlorophyll. He showed that camphor appeared as dextro, levo, and racemic isomers, the same as tartaric acid, and demonstrated that these isomers could be obtained by chemical means. He postulated that a compound appearing in one isomeric form should also be present in the two other forms. He showed that the spectrum of chlorophyll possessed some typical lines, which allowed its detection down to one part in ten thousand, and also when mixed with other substances, fact that provided an important physiological and forensic tool. Together with Dessaignes they separated physalin, the active bitter component of the plant Chinese lantern (*Physalis alkekengi*).

Keywords: camphor; chlorophyll; optical isomers; physalin; spectroscopy.

RESUMEN

Jules-Marie-Augustin Chautard (1826-1901), un científico francés multifacético que comenzó como farmacéutico y luego se convirtió en físico y coleccionista de monedas. Sus principales actividades estuvieron relacionadas con el fenómeno de la polarización de la luz, particularmente en alcanfor y lavanda, y el estudio espectral de la clorofila. Demostró que el alcanfor aparecía como los isómeros dextros, levo y racémicos, al igual que el ácido tartárico, y demostró que estos isómeros podían obtenerse por medios químicos. Postuló que un compuesto que aparece en una forma isomérica, también debería estar presente en las otras dos formas. Demostró que el espectro de la clorofila poseía unas líneas típicas, lo que permitía su detección hasta una parte en diez mil, y también cuando se mezclaba con otras sustancias, hechos que proporcionaban una importante herramienta fisiológica y forense. Junto con Dessaignes separaron la fisalina, el componente amargo activo de la planta linterna china (*Physalis alkekengi*).

Palabras clave: alcanfor, clorofila, espectroscopia; fisalina; isómeros ópticos.

INTRODUCTION

Life and career (Larousse, 1878; Glasser, 1878; Labrude, 1994; Keller and Leroy, 2012)

Fig. 1. Jules-Marie-Augustin Chautard (1826-1901).

Jules-Marie-Augustin Chautard (Figure 1) was born on January 31, 1826, in Vendôme (Loir-et-Cher), the elder son of Constant Charles François Chautard (1797-1870), a pharmacist, and Bathilde Honorine Jourdain (1799-1870). He took his basic education in his hometown and was supposed to manage the business of his father; for this reason, he began an apprenticeship in a local pharmacy. While doing so, he passed his exams for obtaining the degrees of bachelier ès-lettres (1843) and bachelier ès-sciences physiques (1844). He then moved to Paris and began his formal pharmacy studies. In 1847, after earning his degree of pharmacien de 1^{ere} classe, he participated, and won in the first place, a competition for an internship in the Parisian hospitals. In this position, he was attached for some time to the laboratory of Eugène Soubeiran (1797-1858), director of the Pharmacie Centrale des Hôpitaux. In 1848 he was awarded his degree of licencié ès-sciences physiques and the following year, 1849, his degree of licencié ès-sciences mathématiques. Shortly thereafter his resigned his profession of pharmacist, changed his orientation, and postulated and earned the chair of mathematics at the Lycée of Vendôme. Simultaneously, he continued his studies at the Faculté des Sciences of Paris and in 1852 he was awarded his doctorate in physical sciences, after successfully defending a physics thesis about circular polarization and a chemical one about the essence of turpentine (Chautard, 1852c). Shortly thereafter, he moved from the chair in mathematics to the one in physical chemistry in the Faculté des Sciences of Nancy (1853), and eventually became its dean (1873-1876).

Chautard married Marie Jeanne Lucie Piedor (1828-1954) in 1853, who died after giving birth to their son Paul Charles Marie. In 1857 Chautard married Alix Zoé Robillard (1830-1878); four children were born of this union.

Chautard participated actively in professional and public activities. He was member of the Conseil Central d'Hygiène et de Salubrité de la Meurthe (1860); founding member of the Société Archéologique du Vendômois (1861); corresponding member of the Académie Impériale de Metz (1865); member of the Société de Médecine de Nancy (1869); President of the Commission Météorologique de la Meurthe (1864); Cantonal delegate for the inspection of schools (1875). He was elected Officier de l'Instruction Publique (1852) and Officier de l'Académie (1856), two French national orders awarded to distinguished academics and teachers for valuable service to universities, education, and science. He was appointed Chevalier de l'Ordre Pontifical de Saint-Grégoire-le-Grand and Honorary Dean of the Faculté des Sciences at the Université Catholique de Lille.

Chautard passed away in Croissanville (Calvados) on February 17, 1901.

Scientific contribution

Chautard wrote about 55 papers and books (i.e., Chautard, 1862. 1865, 1866, 1869, 1871, 1872a, 1873g, 1875c, 1882) about organic chemistry, chemical synthesis, plant principals, spectral phenomena, numismatics, etc. In addition to the few subjects described below, he demonstrated the presence of butyric acid in the waters obtained in the tanning process (Chautard, 1845); with the physician Victor Dessaignes (1800-1885) they separated neutral calcium malate, butyric acid, and asparagine (Dessaignes & Chautard, 1848); he demonstrated the production of chloroform and other chemicals by the action of calcium hypochlorite on turpentine (Chautard, 1851, 1852ab), the production of toluidine by the action of nitric acid on turpentine (Chautard. 1853a), the production of chloroform by the action of calcium hypochlorite on variety of essences (i.e., peppermint, lemon, rue, anise, lavender, and thyme), oils and resins (i.e., castor oil, rosin) etc. (Chautard 1855a), he synthesized pyroterebic acid (Chautard, 1855b); demonstrated the presence of caproic acid in the flowers of *Satyrium hircinum* (Chautard, 1864a);), etc. Within his work on physical phenomena, he studied the diffraction of very different rays passing through a perforated screen placed in front of a mirror (Chautard, 1861), magnetism and diamagnetism in gases (Chautard, 1867); designed an acoustic pyrometer (Chautard, 1874c); studied the influence of several phenomena on the spectrum of gases rarefied gases (Chautard, 1864b, 1874d, 1875ab, 1876); etc.

Besides his scientific and academic activities, Chautard was passionate for numismatics; besides collecting old coins, he also wrote numerous papers on the subject (i.e., 1872a, 1882).

Camphor

In 1848 Dessaignes and Chautard reported the analysis of the essential oil of chamomile (*Matricaria parthenium*), obtained by distillation of the upper half of the plant, stems, leaves, and flowers (Dessaignes & Chautard, 1848). The small amount of a greenish volatile oil collected, when left alone overnight, deposited large crystalline plates of stearoptene (the more solid portion of a volatile oil, as distinguished from the more fluid portion or eleoptene). The purified stearoptene exuded a strong and pure scent of camphor, melted at 175 °C and boiled at 204 °C. Analyzed by means of copper oxide indicated that it contained, by weight, 78.76% carbon, 10.69% hydrogen and 10.55% oxygen, that is, it was a camphor. The matricaria oil separated from the camphor by the preceding operations, was dried over calcium chloride and analyzed. The results showed that it contained, by weight, 77.60% carbon, 10.17% hydrogen, and 12.03% oxygen, indicating that it was mixed with camphor. When heated, it began boiling at about 205 ºC and most of the oil passed from 205° to 220 °C, leaving a colored residue. The last half of the product, collected from 212º to 220 °C, left a deposit of a large quantity of camphor. Several fractions were separated at different temperature ranges. For example, the oil collected between 160° and 168 °C was found to contain, by weight, 86.46% carbon, 11.58% hydrogen, and 1.96% oxygen. Dessaignes and Chautard concluded that the volatile oil of *Matricaria parthenium* very probably contained, besides camphor, a hydrocarbon of formula C_5H_8 and an oil more oxidized than camphor (Dessaignes and Chautard, 1848).

These data were reported again in Chautard's doctoral thesis with the additional information that the camphor obtained from *Matricaria parthenium* was levorotatory while the one prepared from the *Laurineas* (i.e., *Laurus camphora*) was dextrorotatory (Chautard, 1852c). Now, Chautard reported that by treating this camphor with nitric acid, and by following the precautions indicated for the transformation of ordinary dextrorotatory camphor into camphoric acid, he had isolated a new acid, which deviated the plane of polarization to the left, exactly by the same quantity as the ordinary camphoric acid deflected it to the right. The phenomenon was identical with the one found with two tartaric acids, one deviating the polarized light to the right in the same amount as the other deviated it to the left (in modern terms, *enantiomers*) (Chautard, 1853b). These two acids had exactly the same physical and chemical properties (i.e., solubility, crystalline form, cleavage, etc.). In addition, mixing equal weights of the two acids they combined immediately, providing a new acid quite distinct from its two components, and completely inactive on the polarized light, in other words, a *racemic* camphoric acid. According to Chautard, his results provided a new example of the phenomenon discovered by Louis Pasteur (1822-1895) in tartaric acid (Chautard, 1853b).

In another paper, Chautard described the preparation and properties of camphoric acid inactive by compensation (racemic) and the discovery of camphoric acid *constitutionally* inactive (Chautard, 1863b). The first one was obtained by direct oxidation of racemic camphor, or by mixing in equal weight, the dextro and levo camphoric acids. Both processes produced exactly the same acid. This acid was much less soluble than its congeners: 33% in alcohol, 28% in ether, and 1% in water. The alkaline derivatives were very soluble in water but non-crystallizable. Boiling a mixture of 10 parts of racemic camphoric acid, 20 of absolute alcohol, and 5 of sulfuric acid, left a residue, which diluted with water, separated an oily phase composed of racemic camphoric acid. Upon heating, this oil decomposed into racemic camphoric ester and anhydrous racemic acid. The ester was a very odorous and colorless oil, of relative density of 1.03 at 15 °C, and boiling at 270º to 275 °C. Treatment with a solution of concentrated KOH and boiling regenerated the alcohol and produced an inactive camphoric acid different from the one used for the preparation of the ester. This new acid was pulverulent, non-crystallizable, sparingly soluble in common solvents, had no optical activity, produced non-crystalline combinations with alkaline bases, and sublimated partially while losing water. Elemental analysis indicated that it contained, by weight, 59.7% carbon, 8.6% hydrogen, and 31.7% oxygen. Chautard was unable to determine if the lack of optical activity was due to the specific nature of its molecules, or else, to the fact that it was formed by the union of two substances of opposite rotations (Chautard, 1863b).

In 1857, Chautard published a more detailed study of the preparation and properties of Matricaria camphor and oil, together with some observations relating to lavender camphor, as well as to the action of ordinary sulfuric acid on Japanese camphor (Chautard, 1857a).

As mentioned above, Dessaignes and Chautard had already reported that the essential oil of Matricaria was always of a greenish blue and contained more or less resin coming from the oxidizing action of the air. Purified by distillation, it was levorotatory, clear, colorless, and had no effect on vegetable colors. Its smell was penetrating and unpleasant and its flavor aromatic, with a bitter aftertaste. Subjected to a cold of -4º to -5 °C, it gave numerous crystals which were easy to separate by the filtration and by pressing between several doubles of Joseph paper (Dessaignes and Chautard,1848). The essence of chamomile began to boil below 160 °C, and most of it distilled from 200º to 225 °C. The density as well as the rotatory power of the essence of chamomile varied according to the temperature at which it was collected. For example, the oil distilled below 175 ºC had a relative density of 0.8844 and a rotatory power of -38.51º. At 210º-220 ºC the corresponding values were 0.9690 and -2.34º; above 230 ºC the oil showed a clear dextrorotatory power. These divergent numbers did not allow assigning it a definite composition. Anyhow, it was clear that the essence was united with variable quantities of another dextrorotatory body, boiling from 240º to 250 °C, and probably more oxidized than camphor (Dessaignes and Chautard,1848).

According to Chautard, the most interesting portion of the essence of chamomile was the camphor, which was deposited by cooling. It could be separated from liquid essence by treatment with nitric acid of a density low enough to exert only a negligible action on the camphor. Distilling a mixture of the essence with nitric acid diluted with its volume of water resulted in the release of shining vapors and the total destruction of the oil. Chautard speculated that it was very probable that the ordinary camphor oil of *Laurus camphora*, was only a mixture of solid camphor and a hydrocarbon, isomer of the essence of turpentine, and destroyable by nitric acid. The purified Matricaria stearoptene smelled strongly as pure camphor. It was white, transparent, crystallized by sublimation into small octahedra, it was levorotatory, had a relative density of 0.9853 (18 °C), melted at 175 °C, and began boiling at 204 °C. It was very soluble in alcohol, ether, chloroform, and fixed and volatile oils. Chautard found that the rotatory power of a solution of chamomile camphor in alcohol decreased as the solution became more diluted. Elemental analysis indicated that it contained, by weight, 78.76% carbon, 10.69% hydrogen and 10.55% oxygen (Chautard, 1857a).

Chautard also studied the camphor from lavender. The first thing he did was to confirm Jean-Baptiste Biot (1774-1862) report that the essence of lavender did not deviate the plane of polarization of the light rays (Biot, 1839). This result led to him to ask if it was due to the fact that lavender camphor was inactive according to the specific nature of each of its molecules (components), or because it was formed by the union of two substances with opposite rotations, of the two right camphors and left, which being in equal proportions would give a system devoid of rotary properties (as he had found for chamomile essence) (Chautard, 1857a). To answer this question, he first treated it as he had done with the camphor of chamomile. This turned out to be unsuccessful because the commercial lavender essence was mixed with many substances (among them, turpentine) to lower its price. This forced him to extract by himself the essence from the plant harvested at the time of flowering in the middle of the dry and hot summer of 1854. Cooling this essence at very low temperatures allowed him to separate only small amounts of the camphor. This difficulty was compounded by the fact that dextrorotatory camphor and levorotatory camphor had identical properties. Consequently, he opted for preparing an inactive camphor by mixing equal parts of Japanese camphor and Matricaria camphor. He found that this product had nothing, except the absence of rotary power, which distinguished it from the camphors which formed it. It still looked perfectly like lavender camphor and each component; heated with nitric acid turned into inactive camphoric acid (Chautard, 1857b).

The last subject was investigating the possibility of artificially modifying ordinary straight camphor, so as to alter its rotary power and transform it into inactive camphor (Chautard, 1857ab). This possibility had already been tested by Z. Delalande (Delalande, 1839). Delalande had reported that treating camphor with a large excess of sulfuric acid monohydrate and heated at 100 °C for about an hour, converted it, without releasing SO_2, into a volatile oil having exactly the same composition, the same boiling point, the same density, but differing from ordinary camphor only by its liquidity and a notable decrease of the rotatory power. Digestion of this oil with KOH at about 200 °C turned it into a crystalline product completely identical to natural camphor but endowed with a rotatory power appreciably lower than that of the latter substance, although much larger than that of the oil from which it came (Delalande, 1839).

Chautard applied Delalande's process to a mixture of 250 g of Japanese camphor with one kg of ordinary sulfuric acid. The mixture was heated to 100 °C and samples were taken at different time intervals. Chautard observed that the camphor disappeared little by little, while SO_2 was being released accompanied by a change in the color of the solution. After 12 to 13 hours of continuous exposure of the mixture to a temperature of 100 °C, the remaining oily liquid presented no rotatory power. This oil was purified by repeated washing with a solution of KOH, followed by distillation over calcium chloride. The pure product was colorless, had a slightly aromatic odor, relative density 0.974 (6 °C), did not solidify at -10 °C, and boiled at 240 °C. Treated with boiling nitric acid, it dissolved with the production of nitrous gas; water precipitated from it a soft resin, soluble in alcohol, non-crystallizable. Neither camphor nor camphoric acid occurred in this reaction. This oil was not the only body formed. It was accompanied by a considerable amount of a carbonaceous deposit and a resinous residue (Chautard, 1857ab).

Chautard concluded as follows: (1) under the influence of sulfuric acid the molecular constitution of camphor was completely destroyed; (2) the substance studied by Delalande was actually a mixture of camphor oil and ordinary camphor producing a mixed system whose composition, chemical properties and rotatory power were similar to those of camphor. (Chautard recommended naming it *camphrene*); and (3) any dextrorotary substance had a levorotary and a racemic isomer (Chautard, 1857a).

Chautard wrote that the phenomena of rotatory polarization had become a very powerful tool, which allowed chemists to solve problems of molecular structure, which could not be solved otherwise. Plant physiologists had also found in these phenomena a rapid and easy means of ascertaining the changes, which the age or the nature of the organs brought about in the constitution of the nourishing juices of vegetables. These facts suggested the need to explore the optical behavior of the essential oils present in a wide variety of plants (Chautard, 1863ac).

Although all the essences examined possessed, with very few exceptions, the property of deviating the plane of polarization of light to the left or to the right, in a different degree, no research had been conducted to recognize the possible relation, which may exist between the rotary power of an essence and the portion of the plant which provided it, or the time of the year to which it had been harvested. All essential oils were mixtures in various proportions of several liquids, which differed by their composition or by their point of boiling point. Unfortunately, it was extremely difficult to separate them completely by distillation; they were always obtained more or less mixed, never in a state of perfect purity. Many essences naturally contained a solution of a solid compound (stearoptene) of clearly defined composition and properties dissolved in an oil (eleoptene). Fortunately, the presence or absence, the degree of abundance or scarcity of any of these bodies in a volatile oil, could sometimes be detected by observation of the rotary properties. The oil held in solution varied according to the nature of the essence itself, the part of the plant, the time of harvest, the temperature of the year, humidity, soil, etc. (Chautard, 1863ac).

In the first stage, Chautard studied the essential oil of *Matricaria Parthenium* L., known to produce the largest amount of camphor. This essence was known to contain two perfectly distinct principles: a liquid similar to the essence of turpentine and a solid body identical to the camphor of *Laurinea*. Chautard extracted the essence from different portions of the plant, at different stages of vegetation; (1) from cutting the leaves, when the first buds appeared; (2) from the cutting of leaves, stems and flowering tops; (3) from the whole plant sometime after flowering; (4) from the regrowth of the leaves; (5) from the green stems; (6) of the leaves at the time of flowering; and (7) from tops in full bloom. Each one of these essences was analyzed for amount of essence, boiling point, presence of camphor, relative density, rotary power, and chemical composition. For example, the essence obtained from cutting the leaves when the first buds appeared, was found to start boiling at 150 °C; the portion collected below 200 °C had a rotatory power of -35°, a relative density of 0.889, and contained a very large amount of camphor. Redistilled in a vacuum and analyzed, it gave, by weight, carbon 87.9% and hydrogen 11.8%. The essence obtained from the regrowth of the leaves had rotatory power -12° and contained lesser camphor. Elemental analysis indicated, by weight, carbon 78.7% and hydrogen 10.8%. The essence removed from tops in full bloom did not contain camphor, started boiling above 200 °C, contained a notable proportion of oxygen (13.98%), and was now *dextrorotatory* (+5°) (Chautard, 1863ac).

Chautard determined the rotatory power of the essence of 56 plants pertaining to many families: among them: Composed, Umbellifers, Aurantiacus, Laurineas, Conifers, and Labiacea (Chautard, 1863ac).

Chlorophyll spectra

Chautard carried an extensive and spectroscopic investigation of chlorophyll (Chautard, 1872b, 1873a-g, 1874ab). All the pertinent measurements were made with Duboscq spectroscope where the micrometer was divided into 150 divisions, the 40th of which corresponded to the *D* line of sodium; n°10 coincided roughly with Fraünhofer's *A* line, and n°150 with the *H* line (Chautard, 1873a).

In his first paper (Chautard, 1872b), he reported that the spectra of alcoholic solutions of chlorophyll presented outstanding black bands, the position, number, width, and intensity of which varied within fairly wide limits. Hence, to draw reliable deductions from these data, required formulating exactly the general conditions of the experiment. These conditions depended on the nature of the plant, the different parts of which were neutral, acidic or alkaline, its rank in the plant classification; then, for a given plant, the climate conditions, the temperature, the season of exposure, the soil, and finally the nature of the solvent used (Chautard, 1872b).

Thus, an alcoholic solution of chlorophyll, fresh and strongly colored, gave the following very neat and very distinct phenomena: under the thickness of 6 cm the bright red was manifested from 10 to 18 degrees, with a maximum at about 15 degrees; a very dark black band begun abruptly at 18 degrees, continued up to 50 degrees, degrading its color imperceptibly up to 55 degrees. The absorption was so complete that the sodium line at 10 degrees ceased to be visible when a platinum wire impregnated with a little sodium chloride was introduced into the flame. From 55 degrees on, green was very brilliant and could be seen distinctly up to about 70 degrees, mixed at its extremity with a little blue. The same solution, under the thickness of 2 cm, produced a completely different picture. This time the wide black bland split into two parts, one extending from 18 to 25 degrees, the other from 31 to 36 degrees with orange in the interval, while beyond, the other shades followed one another in the usual order, without any alteration. Here the sodium line no longer underwent absorption. The important fact was that the spectra of more diluted solutions or reduced thickness of the observed layer, presented the same black band, less and less dark, while that of the middle of the red narrowed, while maintaining its center at the same point. This observation was present even when the alcoholic solution contained down to 1/10000 chlorophyll, originating from a wide range of plants, among them, ivy, grasses, spinach, belladonna, foxglove, mosses, green tree leaves, fern stumps, and lilac buds (Chautard, 1872b).

Chautard added that mixing an alcoholic solution of chlorophyll with an organic solution of a different color (i.e., saffron, turmeric, fuchsin, and sunflower) did not prevent the appearance of the specific black line of chlorophyll. A mixture of a diluted solution of blood with another of diluted chlorophyll still showed the two lines specific to the first substance and the specific line of the second. This characteristic was also valid for mixtures of chlorophyll with metallic salts and of chlorophyll taken from the dry leaves used in medicine, such as, belladonna, henbane, aconite, and digitalis (Chautard, 1872a).

As mentioned above, Chautard found that the black band presented by the spectrum of chlorophyll in the middle part of the red (between the lines *B* and *C* of Fraunhofer). was so persistent that it allowed detecting the presence of this substance in a solution which contained only 1/10000 of its weight. This high sensibility allowed the detection of chlorophyll in the residues of digestion and assure that it had not thus undergone any other alteration than that of time or of acids. make him stand naturally (Chautard,1873a).

Chautard promptly realized the possibility of using this singularity in medical and forensic examinations. For this purpose, he treated both human and animal excrement with alcohol and obtained a colored extract, which completely absorbed the most refrangible colors of the spectrum and presented in the medium red and in the orange the two specific lines of chlorophyll, which he had previously discovered. In addition, the green region was often crossed by a black band, which seemed to be connected to the spectrum of the bile, a common component of the feces. An interesting result was that the specific lines of chlorophyll that appeared in the spectrum of the excrement of omnivores (horses, cows, sheep, dogs, cats, rabbits, chickens, etc.) was somewhat less clear than the ones appearing in that of the herbivores. Further experiments showed that feeding dogs and cats exclusively on meat for several days resulted in a weaker or complete disappearance of the black, red line of the spectrum. Chautard mentioned that the characteristic lines of chlorophyll also appeared in an alcoholic tincture of cantharides; they originated from the leaf debris contained in their feed (Chautard, 1873a).

In 1860, Edmond Frémy (1814-1894) wrote that chlorophyl was considered one of the most important substances of the vegetable kingdom. Many publications had referred to its constitution and chemical properties. Some chemists regarded it as an immediate principle, others believed that the coloration of the leaves was due to a mix of many different substances; some believed that it contained nitrogen, others, that it was a ternary substance (Frémy, 1860). The conflicting evidence led Frémy to conduct his own experiments to determine the composition of chlorophyll and find if it was a simple component or if its color originated from a mixture or the combination of a blue body with another yellow. For this purpose, Frémy used alumina hydroxide, a substance having an affinity for coloring substances, which could be increased or decreased by addition of water or absolute alcohol. His results indicated that the pertinent extract was yellow or yellow green, depending on the dilution of the solution. In this manner, he was able to split the chlorophyll color into a yellow and a blue substance, which he named *phyloxanthine* and *phylocyani*n, having a different affinity for alumina hydroxide. In the next stage, Frémy tried to decompose the combination of the hydroxide with the colors, using a variety of reagents, among them, absolute alcohol, ether, carbon disulfide, and HCl. The best reagent turned out to be ether and HCl. Frémy also studied the coloration the leaves in the different seasons of the year (Frémy, 1860).

Chautard believed that the action of alumina hydroxide on chlorophyll could be easily characterized using a spectroscope and other alkalis. His results justified this assumption and added valuable information to the phenomenon (Chautard, 1873b).

For example, treating an alcoholic solution of chlorophyll with a few drops of a solution of KOH or ammonia did not produce changes, the color of the solution and the four bands in the first region of the spectrum remained unaltered at all. The result with hot KOH was completely different: the specific black band of red split into two lines, fixed in position, but whose width and intensity depended on a more or less prolonged action of the alkali; the other lines peculiar to chlorophyll disappeared almost completely. Chlorophyll, known to be sparingly soluble in water, became more soluble, yielding a dark olive tint. This resulted in the doubling of the black line specific to red; a first portion appeared from 19 to 22 degrees of the micrometer, and second, a from 26 to 29 degrees (Chautard. 1873b).

Chautard separated the leaves left from the water extract and treated them with alcohol. The filtrate was mixed with a few drops of concentrated acetic acid and then examined in the spectroscope: now the double line had disappeared, the two black bands become one. Addition of a little ammonia reversed the result: the two bands reappear as before. This cycling phenomenon could be repeated several times. Surprisingly, leaving the ammonia solution alone for a few hours resulted in the appearance of a third band, at around 18 degrees. Ammonium sulfide produced the same results (Chautard, 1873b).

Chautard also studied the action of rays of different colors (Chautard, 1873c) and the influence of the solvent (i.e., ether, chloroform, essences, mineral oils, carbon disulfide, etc.) (Chautard, 1873d), on the spectrum of chlorophyll, as well as the presence of and accidental (Chautard, 1873e) and supernumerary rays (Chautard, 1874b).

Chautard summarized all his work about the spectrum of chlorophyll in a long (56 pages) paper (Chautard, 1874a) and two books (Chautard, 1873g, 1875c).

Chinese lantern (*Physalis alkekengi*)

Dessaignes and Chautard wrote that a few physicians had used the plant Chinese lantern to successfully combat intermittent fevers, although it was not known if it contained a febrifuge principle, which could serve as a substitute for quinine. This was a challenging possibility, which Dessaignes and Chautard decided to test (Dessaignes & Chautard, 1852).

It was known that all parts of the plant were bitter, especially the leaves and capsules that enveloped the fruit. In a first experiment, Dessaignes and Chautard extracted the dry leaves with alcohol and evaporated the extract to dryness in a water bath. The resulting residue was bitter and colored green by a large amount of chlorophyll. This process was repeated with cold water; The extract, brown and bitter, was treated with animal charcoal to eliminate the bitterness, followed by washing, drying, treatment with pure boiling pure alcohol, and finally, evaporation to dryness. The small amount of residue was yellow-brown and very bitter. In a third experiment, the aqueous solution was treated with KOH and then stirred with chloroform (about 20 g per liter of solution). The resulting almost white precipitate was separated by filtration, which after washing and drying, left a pulverulent residue, very little colored and bitter, which did not contain nitrogen and did not behave with acids like organic alkaloids (Dessaignes & Chautard, 1852).

Dessaignes and Chautard found that complete removal of the bitterness of the aqueous solution required repeated treatments with chloroform. The extracted bitter principle was purified by dissolving in hot alcohol, adding a little of animal charcoal, precipitating the filtered liquor with water, and washing the precipitate with cold water on a filter. The purified bitter matter, which Dessaignes and Chautard named *physalin*, appeared as a light, white powder, slightly tinted yellow tinge, non-crystalline, having a persistent bitterness, slightly soluble in cold water and a little more in boiling water, sparingly soluble in ether, and soluble in chloroform and hot alcohol. It softened around 180 °C and at 190 °C turned into a molten pasty; then it became colored and filled with bubbles. It burned with a sooty flame and without leaving any residue. Physalin was little soluble in diluted acids; heated with KOH, it did not release ammonia. it was soluble in hot ammonia but was precipitated from its alcoholic solution by ammoniacal silver nitrate in the form of a fluffy and yellowish precipitate, having the approximate formula $C_{28}H_{30}O_9.3PbO$. Dessaignes and Chautard added that the extract of the ripe berries had a pleasant acidity, mixed with bitterness due to citric acid (Dessaignes & Chautard, 1852).

BIBLIOGRAPHIC REFERENCES

Biot, J. B. (1839). Note sur l'Huile Isomère du Camphre Naturel. *Compt. Rendus, 9*, 621-626.

Chautard, J. (1845). De l'Existence de l'Acide Butyrique Libre dans le Tannée. *J. Pharm., 7,* 454-457.

Chautard, J. (1851). Note sur la Production du Chloroforme à du Chlorure de Chaux et de la Essence de Térébenthine. *Compt. Rendus, 33*, 671-672.

Chautard, J. (1852a). Étude de l'Action de Hypochlorite de Chaux sur l'Essence de Térébenthine et quelque autres Huiles Essentielles. *J. Pharm., 21*, 88-94.

Chautard, J. (1852b). Note sur quelques Produits Obtenus de l'Essence de Térébenthine. *Compt. Rendus, 34*, 485-487.

Chautard, J. (1852c). *Essais de Polarisation Circulaire et Monographie de l'Essence de Térébenthine.* Thèses de physique et de chimie présentées à la Faculté des Sciences de Paris, l'août 1852 par Jules Chautard. Lemercier, Vendôme.

Chautard, J. (1853a). Sur un Nouveau Mode de Production de la Toluidine. *J. Pharm., 24*, 166-168.

Chautard, J. (1853b). Mémoire sur l'Acide Camphorique Gauche et sur le Camphre Gauche. *Compt. Rendus., 37*, 166-167.

Chautard, J. (1855a). Nouvelle Observations Relatives à l'Action du Chlorure et du Bromure de Chaux sur les Substances Organiques. *J. Pharm., 28*, 179-183.

Chautard, J. (1855b). Note sur Deux Nouvelles Séries d'Acides Organiques Homologues, et sur la Constitution de l'Acide Pyrotérébique. *J. Pharm.*, *28*, 192-196. Published as booklet by Vve Raybois, Nancy.

Chautard, J. (1857a). Nouvelles Recherches sur les Propriétés Optiques des Différents Espèces de Camphre et en Particulier sur celles du Camphre de Matricaire. *Mém. Acad. Stanislas*, 206-222.

Chautard, J. (1857b). Action de l'Acide Sulfurique Monohydraté sur le Camphre de Japon. *Compt. Rendus*, *44*, 66-68.

Chautard, J. (1861). Note sur les Phénomènes de Diffraction Obtenus par le Passage de Rayons très Divergents à Travers un Écran Percé d'un Certain Nombre d'Ouvertures et Placé Devant l'Objectif d'une Lunette. *Mém. Acad. Stanislas*, 346-349. Published as booklet by Ve Raybois, Nancy.

Chautard, J. (1862). *De la Vulgarisation de quelques Phénomènes de Physique Expérimentale.* Ve Raybois, Nancy.

Chautard, J. (1863a). Nouvelles Études due le Camphre Gauche de Matricaire et sur les Huiles Essentielles au Point de Vue de la Production de Camphre. *J. Pharm., 44.* 13-33.

Chautard, J. (1863b). Note Relative aux Acides Camphoriques Inactifs. *Compt. Rendus. 56*, 698-670.

Chautard, J. (1863c). De la Recherche du Camphre dans les Huiles Essentielles Indigènes. *Mém. Acad. Stanislas*, 378-405.

Chautard, J. (1864a). Note sur la Présence de l'Acide Caproïque dans les Fleurs du *Satyrium Hircinum*. *Compt. Rendus, 58*, 639-641.

Chautard, J. (1864b). Phénomènes Observés dans les Spectres Produits par la Lumière des Courants Traversant les Gaz Raréfiés. *Compt. Rendus, 59*, 383-384.

Chautard, J. (1865). *Mémoire sur les Divers Acides Camphorique suivi de Deux Notes*: *l'Une sur les Acides de l'Orchis Hyrcinum*: *l'Autre sur les Propriétés Phosphogéniques de la Lumière du Magnésium.* Ve Raybois, Nancy.

Chautard, J. (1866). *Exposé Théorique et Pratique des Sources de Chaleur et de Lumière*. Grosjean, Nancy,

Chautard, J. (1867). Expérience Relatives au Magnétisme et au Diamagnétisme des Gaz. *Compt. Rendus, 64*, 1141-1142.

Chautard, J. (1869). *De la Météorologie Agricole*. Sordoillet, Nancy.

Chautard, J. (1871). *Du Rôle de la Science dans la Guerre de 1870-1871.* Sordoillet, Nancy.

Chautard, J. (1872a). *Imitations de quelques Types Monétaires Propres à la Lorraine et aux Pays Limitrophes.* Crépin-Leblond, Nancy.

Chautard. J. (1872b). Recherches sur le Raies de la Chlorophylle. *Compt. Rendus, 75*, 1836-1839.

Chautard, J. (1873a). Examen Spectroscopique de la Chlorophylle dans les Résidus de la Digestion. *Compt. Rendus, 76*, 103-105.

Chautard, J. (1873b). Modifications du Spectre de la Chlorophylle sous l'Influence des Alcalis. *Compt. Rendus, 76*, 570-572.

Chautard, J. (1873c). Influence des Rayons de Diverses Couleurs sur le Spectre de la Chlorophylle. *Compt. Rendus, 76*, 1031-1033.

Chautard, J. (1873d). Examen des Différences Présentées par le Spectre de la Chlorophylle selon la Nature du Dissolvant. *Compt. Rendus, 76*, 1066-1069.

Chautard, J. (1873e). Classification des Bandes d'Absorption de la Chlorophylle. *Compt. Rendus, 76*, 1273-1275.

Chautard, J. (1873f). Recherches sur le Spectre de la Chlorophylle. *Compt. Rendus, 77*, 595-597.

Chautard, J. (1873g). *Quelques Mots sur les Raies de la Chlorophylle et leurs Application en Physiologie, en Toxicologie et en Pharmacie*. Levrault, Nancy.

Chautard, J. (1874a). Recherches sur le Spectre de la Chlorophylle. *Ann. Chim. Phys*. [4], *3*, 1-56.

Chautard, J. (1874b). Nouvelles Bandes Surnuméraires Produits dans les Solutions de Chlorophylle, sous l'Influence d'Agents Sulfurés. *Compt. Rendus, 78*, 414-416,

Chautard, J. (1874c). Pyromètre Acoustique. *Compt. Rendus, 78*, 128-129.

Chautard, J. (1874d). Action Exercée par un Électro-Aimant sur les Spectres des Gaz Raréfiés, Traversés par des Décharges Électriques. *Compt. Rendus, 79*. 1123-1124.

Chautard, J. (1875a). Action des Aimants sur les Gaz Raréfiés Renfermés dans des Tubes Capillaires et Illuminés par un Courant Induit. *Compt. Rendus, 80*. 1161-1164.

Chautard, J. (1875b). Phénomènes Magnéto-Chimiques Produits au Sein des Gaz Raréfiés dans les Tubes de Geissler, Illuminés à l'Aide de Courants Induits. *Compt. Rendus, 81*, 75-77.

Chautard, J. (1875c). *Spectres de la Chlorophylle et leurs Applications à la Chimie à la Physiologie, à la Toxicologie*. Berger-Levrault, Paris.

Chautard, J. (1876). Actions Magnétiques Exercés sur les Gaz Raréfiés des Tubes de Geissler (Quatrième Note). *Compt. Rendus, 82*, 272-274.

Chautard, J. (1882). *Jetons des Princes de Vendôme de la Deuxième Maison de Bourbon*. Lemercier, Nancy.

Delalande, Z. (1839). Recherches sur le Camphre et la Coumarine u Stéaroptène des Fèves de Tonka. *Compt. Rendus, 9*, 608.

Dessaignes, V. (1850). Formation de l'Acide Aspartique avec le Bimalate d'Ammoniaque, *Compt. Rendus*, *30*, 324-325.

Dessaignes, V. and Chautard, J. (1848). Observations de Chimie Organique. *J. Pharm., 13*, 241-250.

Dessaignes, V. and Chautard, J. (1852). Note sur le Principe Amer de l'Alkékenge. *J. Pharm., 21*, 24-26

Frémy, E. (1860). Recherches sur la Matière Colorante Verte des Feuilles. *Compt. Rendus, 50*, 405-412.

Glaeser, E. (1878). *Biographie Nationale des Contemporains*. Page 116, Glaeser, Paris.

Keller, V. and Leroy, J. (2012). *Le Transfèrement de l'École Supérieure de Pharmacie en 1872. Biographie de Deux Érudits de Passage à Nancy*: *Charles Ernest Schmitt et Jules Chautard.* Thèse présentée et soutenue publiquement le 14 décembre 2012 pour obtenir le Diplôme d'Etat de Docteur en Pharmacie, Faculté de Pharmacie, Université de Lorraine.

Labrude, P. (1994). La Contribution des Pharmaciens à la Création (1887-1892) et à l'Enseignement de l'Institut Chimique de Nancy. L'Influence des Systèmes Étrangers d'Éducation sur cette Création. *Rev. Hist. Pharm., 82*(302).

Larousse, P. (1878). *Grand Dictionnaire Universel du XIXe Siècle*. Administration du Grand Dictionnaire Universel, Paris. Vol 16, Supplément, p518.

This article does not present a conflict of interest