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BIBLIOGRAPHIC REVIEW

# ARMAND JEAN FRANÇOIS SÉGUIN

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## ABSTRACT

Armand Séguin (1767-1835), a French self-educated chemist and physiologist, who learned chemistry and sciences while working for Lavoisier, carried on extensive work about physiological phenomena such as respiration, transpiration, and the action of the inhaling and exhaling vessels of the human body. Together with Fourcroy and Vauquelin, he demonstrated that water was composed of hydrogen and oxygen. He also studied the composition and properties of several natural products, such as cinchona, opium, rosin, coffee, and cinnabar, and the process of vegetation under special conditions. His most important contribution was the development of a new tanning process, which shortened the results from years to a few days. This achievement made him immensely rich and famous.

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

## RESUMEN

Armand Séguin (1767-1835), químico y fisiólogo autodidacta francés, que aprendió química y ciencias mientras trabajaba para Lavoisier, llevó a cabo un extenso trabajo sobre fenómenos fisiológicos como la respiración, la transpiración y la acción de inhalar y exhalar de los vasos del cuerpo humano. Junto con Fourcroy y Vauquelin, demostró que el agua estaba compuesta de hidrógeno y oxígeno. También estudió la composición y propiedades de varios productos naturales, como cincona, opio, colofonia, café y cinabrio; y estudió el proceso de la vegetación en condiciones especiales. Su aportación más importante fue el desarrollo de un nuevo proceso de curtido que acortó el resultado de más de varios años a unos pocos días. Este logro lo hizo inmensamente rico y famoso.

**Palabras clave:** café; cinchona; cinabrio; colofonia; composición del agua; opio; respiración; salubridad; vegetación.

# INTRODUCTION

## **Life and career** (Partington, 1962; Pierson, 2008)

Armand Jean François Séguin was born in Chartres, on March 21, 1767, the son of Hector Hyacinth Séguin the administrator of the duke of Orléans, and Marie Anne Madeleine Chancerel. No information seems to be available about his early life and education. Anyhow, sometimes in the 1790's he managed to obtain a position of research assistant with Antoine Lavoisier (1743-1794). Clearly, Séguin was a very smart person, who learned rapidly and understood the significance of his results; very soon he was carrying on independent work, the results of which he read to the French Académie des Sciences. Unfortunately, the political events in France at that time resulted in the publication of his results several years later. As a side activity, he started tanning leather, and this led him to develop a new procedure, which shortened the length of the process from years to a few days. The political and international situation of France led him to become the national provider of leather, a position that made him very rich. The Comité de Salut Public generously provided him with all possible facilities, including economic help and valuable land for building his factories, including the island of Sèvres (Île Séguin). In his later years he started to write essays about public economy, fiscal policy, and horse breeding.

In 1795 Séguin married to Marie (Emilie) Félicité Raffard de Marcilly; two children were born of this union, Zoé (1797-1877) and Abel (1799-1873).

Séguin passed away in Paris, on January 24, 1835.

## Scientific contribution

Séguin wrote more than 25 papers about his research activities in organic, inorganic, and analytical chemistry, chemical synthesis, plant principles, etc. He also wrote more than 100 books about public economy, fiscal policy, and horse breeding (i.e., Séguin, 1819, 1829, 1830). In addition to the few subjects described below, Séguin discussed caloric and its different effects, as well as reflections on the theories of Black, Crawford, Lavoisier, and Laplace on animal heat and on the heat released during combustion (Séguin, 1789, 1790, 1791c); with Lavoisier he studied the phenomenon of transpiration and respiration in animals (Lavoisier & Séguin, 1790, 1793, 1814). Séguin discussed the concepts of sensation, cold and heat (Séguin, 1791b); respiration and animal heat (Séguin, 1799); suggested that meteorites did not come from outer space but were simply very small pieces of matter floating in the upper atmosphere, which storms, electrical discharges, etc., caused them to come together and fall upon the earth as larger masses (Séguin, 1813); discussed the properties and effects of the exhaling and inhaling vessels present in human body (Séguin, 1814ci); discovered a new triple salt of sulfuric acid, sodium, and ammonia (without identifying its formula) (Séguin, 1814f); developed a process for the purification of alums (Séguin, 1814j); suggested the use of gelatin as a febrifuge, instead of cinchona, describing many medical cases proving his claim (Séguin, 1815k); etc.

Séguin's important work on tanning will not be presented here, as it has been amply discussed in the literature (Leliévre & Pelletier, 1797).

### *Composition of water*

In 1790, Séguin and Seguin, Antoine-François Fourcroy (1750-1809), and Louis Nicolas Vauquelin (1763-1829) read to the Académie des Sciences two memories reporting their research on the composition of water, determined by burning a mixture of hydrogen and oxygen in closed vessels (Séguin, 1791a; Fourcroy, Vauquelin, and Séguin, 1791).

The authors obtained the oxygen from the thermal decomposition of potassium chlorate (the gas produced was found to contain less than 3% of nitrogen), and the hydrogen from the reaction between zinc and diluted sulfuric acid. Both gases were bubbled through caustic alkali to eliminate any carbon dioxide they may had contained. The combustion of the clean mixture was carried on as slowly as possible, so that any small portion of nitrogen present might not be combined with oxygen. The experiment continued 185 hours without interruption. The quantity of hydrogen employed amounted to 25980.563 cubic inches, and of oxygen, 13475.198 cubic inches, measured at 12.1 °C and 711.20 mmHg. There remained in the balloon a quantity of gas, which amounted to 987 cubic inches, and which on examination was found to contain 467 cubic inches of nitrogen, 39 of $CO_2$, 465 of oxygen, and 16 of hydrogen. After making the proper correction for the quantity of hydrogen, which remained after the combustion, and for the quantity of carbon contained in the hydrogen that was consumed, and which had formed $CO_2$, and after making a similar correction for the quantity of oxygen, which remained, and for the quantity of it that had been spent in the formation of $CO_2$, it appeared that the amounts of hydrogen and oxygen that had combine to form water, where (Séguin, 1791a) (Table 1)

**Table 1**. Hydrogen and oxygen that had combine to form water

| | Cubic inches | | Weight, grams |
|---|---|---|---|
| Hydrogen, | 25963.563 | | 67.3493 |
| Oxygen | 12570.942 | | 402.3927 |
| | | Total weight | 469.7420 |

The ratio of volumes is 2.06, indicating that water is $H_2O$. The quantity of water produced was found to be 7245 cubic inches, so that the deficit amounted to only 4.227 cubic inches.

The Académie des Sciences appointed a committee of experts composed by Pierre-Simon Laplace (1749-1827), Lavoisier, Mathurin Joseph Brisson (1723-1806), and Jean Baptiste Meusnier (1754-1793) to verify the claims of Séguin and his colleagues. The committee repeated the experiences and found the same results. In addition, they examined the water obtained and found that it showed no sign of acidity, not reddening in the slightest manner paper tinged with the infusion of violets or of tournesol. It also had the same specific gravity as distilled water. Mixed with highly pure silver nitrate, it formed no precipitate. The residual gas left in the retort, hardly troubled limewater, indicating the presence of a slight amount of $CO_2$, most probably originating from the carbon present in the hydrogen. It also contained slight amounts of nitrogen and oxygen. (Laplace et al., 1790).

The referees were of opinion that the results of Séguin demonstrated clearly that water was composed of hydrogen and oxygen only (Laplace et al., 1790).

## *Eudiometry and respiration*

According to Séguin (and to the knowledge at his time), eudiometry was a technique for determining the degree of wholesomeness of breathing fluids. Proper practice of eudiometry required, (1) knowing which were the substances which were favorable, and which were those which were harmful to the respiration, and (2) to be able to determine with appropriate instruments, the principles that constituted the composition of the breathable fluids on which eudiometry operated (Seguin, 1791d). Unfortunately, the state of the art did not allow to fulfil these conditions. The methods available allowed only to *compare* samples of air, that is, to determine which was the breathable air that contained more vital air (oxygen) than others. But was this parameter enough to determine the degree of healthiness of any breathable fluid? Wouldn't it be necessary, to complete the picture, to know the noxious air that it could hold in dissolution, and over which, however, we did not have control (Seguin, 1791d)? Everyone was aware that entering a room full of people resulted in the immediate smelling of a suffocating odor, and that eudiometric analysis of this infested air and of the surrounding atmospheric air resulted in a very small difference in the proportions of the principles, which constituted these breathable fluids. Nevertheless, these inconveniences were not a reason for rejecting eudiometry, they constituted a challenge to extend and perfect it (Séguin,1791d).

Séguin wrote that the first eudiometric method was proposed by Joseph Priestley (1733-1804), who based it on the property of nitrous gas of absorbing the vital air contained in breathable fluids. This proposal was followed by many others, for example. Alessandro Volta (1745-1827) suggested a eudiometer based on the detonation of hydrogen gas and Carl Wilhelm Scheele (1742-1786) a lengthy one using sulfides. Unfortunately, these suggestions provided only a relative comparison between different samples of air. Improved answers had been suggested by chemists such as Louis-Bernard Guyton de Morveau (1737-1816), Antoine-Laurent Lavoisier (1743-1794), Antoine-François Fourcroy (1750-1809), and Louis Nicolas Vauquelin (1763-1829), based on the combustion of phosphorus and pyrophore, to determine the proportions, which existed between the vital air and the nitrogen present in the atmosphere (Séguin, 1791d).

Séguin used the experience he had acquired working with Lavoisier on the phenomenon of respiration to develop a eudiometer, which allowed calculating the volume of vital air, which a breathing fluid contained (Séguin, 1791d). The apparatus consisted of a glass or crystal glass cylinder, about 2.5 cm in diameter, and 18 to 20 cm height, closed at the top and flared at its bottom, which was filled with mercury. A small piece of phosphorus was passed through it, which, by virtue of its lower specific gravity, rose to the upper part. This phosphorus was melted using a red carbon, which was positioned closer from the outside of the bell. A known volume of the air to be tested was slowly bubbled into the tube. After the end of the combustion, the contents were left to cool and then the gas passed through a calibrated small bell. The difference of the two volumes indicated the quantity of vital air held by the air subjected to the experiment. Séguin added that his eudiometric method was very fast, very exact, very inexpensive, and finally, as perfect as it was possible to be, when the only objective was to determine the volume of the gases, which entered the composition of the breathable fluids (Séguin, 1791d).

The success with the eudiometer led Séguin and Lavoisier to use it to determine the salubrity and insalubrity of atmospheric air in its various degrees of purity. For this purpose, they requested and received the collaboration of the Parisian St. Denis Hospital. From it, they selected the largest hospitalization room, heavily occupied by 175 female patients (Séguin, 1814b).

The pertinent experiment consisted in closing in the evening all the doors and windows of the room and opening them the next day at five in the morning. As expected, they found the room full of a foul odor. Séguin and Lavoisier distributed their vials full of mercury in various places in the dormitory, including the external space, to compare the quality of the air they contained. Analysis made on the mercury tank with KOH and with Séguin's phosphoric eudiometer indicated that the air in the room, compared to that outside, differed in that it also contained 0.96% of $CO_2$, and 81% of nitrogen. Air samples taken from the upper and lower part of the dormitory showed only almost imperceptible differences in their composition. Séguin and Lavoisier carried the same experiment on the air in a room in the Ste. Ursule Hospital, housed by 142 women. The only difference that this second room instead of being only 2.4 m high, like the St. Denis dormitory, was 3.9 m high. This time they found that the differences between the inside and the outside airs were a 96% for nitrogen, and 0.09% for $CO_2$. Séguin carried a third experiment on the air of a room in the Bicêtre Hospital. Analysis of this air, made with care, proved that it only contained a thirty-ninth of nitrogen, and a fifty-eighth of $CO_2$ (Séguin, 1814b).

Additional experiments carried in all the theaters of Paris on days when the crowd of spectators was very numerous, sampled and analyzed the air on almost every floor and on different floors, moments of the performance, etc. The results were very similar; the proportions of the nitrogen, of oxygen, and of the $CO_2$ of the interior air, were very nearly the same as those of the surrounding air (Séguin, 1814b).

Séguin was surprised to find in all these experiments, and mainly in those which had been made at the dormitory of St. Denis, only such a small quantity of $CO_2$. He verified the correctness of his findings, as follows: The volume of the air contained in the dormitory of St. Denis was 36684 cubic feet; it was known that an ordinary individual exhaled from its lungs about a third of a cubic foot of $CO_2$ per hour; from which it resulted that during seven hours, there had come out of it from the lungs of each woman 2 cubic feet, and consequently that the one hundred and seventy-five women had furnished about 408 cubic feet, number which formed one eighty-ninth part of the air contained in the dormitory, and which closely approximated the result indicated by the analysis of the air in the dormitory, since this analysis indicated up to one ninety-eighth the excess of $CO_2$ in the air in the room, compared to the outside air. Previous experiences already indicated Séguin that it was not to the increase in nitrogen or to the increase in $CO_2$ that the unhealthy air in the St. Denis dormitory could be attributed, and the discomfort that one generally experienced after a certain time in theaters, as well as in large assemblies, when there was not, a continual current of air. The question remained unanswered: what was the cause of this insalubrity and the foul odor felt in the two hospitals rooms (Séguin, 1814b)?

Séguin decided that one way to answer the question was to prepare synthetic mixtures of airs and test them on himself and one of his students. The proper experiments were conducted in a special room having windows, which were well glued with trips of paper and the door trimmed with strips of sheepskin and covered with a thick curtain which applied to it exactly. Care was taken to carry all the experiments under conditions as similar as possible, including the pulse count of the patient. Among the factors studied were the room temperature and humidity (placing water receptacles everywhere and using a hygrometer). The results indicated that none of these factors directly influenced the sensations, which some people experienced in large assemblies. The partial results indicated that these sensations did not seem to come from the degree of temperature, from the degree of humidity, from the proportion of $CO_2$, or from the relative increase of nitrogen (or what amounts to the same, from the relative decrease of oxygen). Séguin could only reasonably attribute them to other substances or other influences (Séguin, 1814b).

Séguin noted that the behavior of his student varied according to the material used by theatres for the purpose of illumination. One possibility was that the unburned oil spreading into the surrounding air produced in large part this difference in sensation. Séguin decided to try synthetic mixtures having increasing amounts of possible noxious substances, because he was less sensitive than his student. The experiments were conducted in the same apparatus that he and Lavoisier had used in their research on respiration. A large bell was filled with atmospheric air mixed with a determined quantity of noxious fluid. Séguin was equipped with a copper mask connected by a tube to the bell to breathe the air located on the upper part of the bell and made his exhalation through caustic alkali. Measurements included the time of his first and last breaths, the pulse every minute, the effect of perspiration, manure, etc. Each experiment lasted about 22 minutes (Séguin, 1814b).

The first results indicated that it was possible to entirely remove the nitrogen contained in the atmospheric air, without rendering it unhealthy, and that pure oxygen was just as healthy as atmospheric air, and produced, relative to respiration, effects absolutely like those observed in the latter, provided that the patient was healthy. Experiments were done with air containing different amounts of $CO_2$; the effect of this gas began to be noticed only when its concentration was about 13%, afterwards it became more and more unhealthy, and finally led to suffocation when it reached 20%- to 25% of the air breathed. Initially, nitrogen could be substituted by hydrogen without producing a very marked effect on the lungs; but afterwards, it caused a discomfort in the respiration.

Séguin mentioned that a mixture of atmospheric acid and 10% hydrocarbon made him lose consciousness. Repetition of these experiments with guinea pigs showed that air mixed with a very small of amount hydrocarbon was enough to asphyxiate them (Séguin, 1814b).

## *Vegetation*

Séguin wrote that plants had the ability of restoring the air altered by our breathing and by combustion, fermentations, and many other operations that modified the composition of the atmosphere. The whole of our existence required as first condition a temperature of about 30 °C degrees, which was maintained by the slow combustion, which took place in our lungs of a portion of carbon and hydrogen, then expelled during the exhalation. The plants, aided by contact with the rays of the sun, captured this carbon and this hydrogen, and by unknown reactions restored the air to its initial qualities. Without this effect, we would soon be surrounded by a fluid whose breathability would destroy all living matter on our globe (Séguin, 1814a).

Animals fed on plants, which they transformed in their interior; part of this food was used for growth, another for maintaining by combustion the temperature necessary for the existence of almost all living beings, and a third was discarded as superfluous. Plants, for their part, fed on the carbon, hydrogen, water, and $CO_2$, which animals returned back; they kept the carbon and the hydrogen and transformed them into substances necessary for their existence, and they rejected a large part of the oxygen, Séguin was aware that all plants were able to appropriate only the substances, which were necessary for them, to elaborate them on their surface or in their interior, and to reject what was useless to them (Séguin, 1804a).

Like animals, plants had four clear functions: respiration, transpiration, nutrition, and reproduction; like them they enjoyed, at least for the most part, this property, which constitutes life, irritability. This allowed making on plants experiments like those which were made on animals, to examine separately each of the four functions, to separate the causes which concurred on them, to isolate their effects, and to submit them to an analysis as exact as that achieved when operating on animals (Séguin, 1814a).

All this information induced Séguin to investigate not only the changes, which plants underwent during their growth, but also those caused by the substances, which surrounded them, or into which they were immersed. The pertinent experiments were conducted with ordinary onions, hyacinth onions, and crocuses, as much as possible of equal strength. Each onion was weighted at the beginning and at the end of each experiment. The pertinent bulbs were submerged in three different aquatic environments: (1) waters colored by the action of Indian wood, saffron, Brazilian wood, madder, cochineal, orchil, gaura, alkanet, indigo, cupric acetate, cupric sulfate, cinchona, gallnuts, and manure; (2) waters scented by lemon, fennel, chamomile, lavender, marjoram, basil, rosemary, thyme, iris, orange blossom, anise and rose; (3) solutions of salts and other substances, for example, mercuric chloride, potassium chloride, white arsenic oxide, zinc sulfate, sodium sulfate, sodium chloride, potassium nitrate, ferrous sulfate, magnesium sulfate, and gallnut (Séguin, 1814a).

Séguin observed the following effects: (1) The colored liquors did not rise in plants by the roots and did not color the flowers of these plants. He thought it was possible that at the end of these roots, and perhaps even on their surface, there was a separation of the water and the coloring part; the water rose in the plant while the coloring matter remained on the roots; (2) scented water had no influence on the scent of the different plants, which suggested again that the roots let only the water go through or that during the circulation the waters fragrances decomposed and changed in nature; (3) all liquors which were poison for animals were also fatal for plants, showing again the remarkable analogies, which existed between animals and plants; (4) substances, which were not fatal for plants were all the more harmful to vegetation as their solution was more concentrated; (5) air contact was necessary for vegetation; deprived of it they vegetated poorly, or not at all; (6) contact with the air alone was not enough, it had to be accompanied by contact with water and a variety of substances appropriate for growth; (7) although plants, in general, were composed only of carbon, hydrogen, nitrogen and oxygen, they failed to vegetate if their roots were immersed in alcohol or in oil; (8) when plants vegetated well, they did not impart an odor to the waters in which they grew, but when their vegetation was not complete, they more or less putrefied these waters, an effect which, moreover, only took place after the annihilation of the irritability of the plant (Séguin, 1814a).

## *Cinnabar*

Séguin wrote that commercial cinnabar was a compound of sulfur and mercury, imported from Holland, which was used in large quantities in painting. These facts led him to study the possibility of manufacturing it in France. To do so, he decided first to determine the intimate nature of cinnabar and the proportion of its principles (Séguin, 1814d).

Sulfur and mercury were known to combine in various proportions to yield two very different compounds, one black, known as *ethiop* (a dark colored chemical compound) the other red, known as *cinnabar* or vermilion. To obtain ethiop, it was enough to triturate a mixture of mercury and sulfur. In this compound, sulfur and mercury had only a weak adhesion, and were rather mixed than combined. Cinnabar could be simply prepared by sublimating or burning ethiop to deprive it of the excess of one of its principles. In this compound, the combination of mercury and sulfur was much stronger than in the original mixture. The information regarding the composition of both substances was conflicting, some scientists, such as Fourcroy, believed that ethiop and cinnabar contained also oxygen combined with mercury while Claude-Louis Berthollet (1748-1822) claimed that ethiop contained hydrogen sulfide, which was released upon heating and transformed into cinnabar. There was also confusion regarding the proportion of sulfur and mercury in each compound. To test the presence of oxygen, Séguin heated a mixture of dry powdered sulfur with well-dried mercury in a thick glass retort for several hours, out of contact with air. At the end, he obtained very fine cinnabar and no hydrogen. This result proved that cinnabar did not contain oxygen, since on the one hand, the mixture of sulfur and mercury had not been in contact with atmospheric air, and on the other, there was no portion of water decomposed during the formation of cinnabar. The same process was conducted under lower heating; this time the product was ethiops and no hydrogen, proof that there was no decomposition of water, and consequently that also the ethiop did not contain oxygen. To test the claim of Berthollet, Séguin prepared ethiop in the ordinary way, that is, by pouring little by little, in the open air, mercury into the melted sulfur, and stirring the mixture without letting it ignite. Afterwards, the ethiop was heated strongly enough to transform it into cinnabar, but without generating any hydrogen sulfide. All these results negated Fourcroy and Berthollet that ethiop and cinnabar contained other elements in addition to sulfur and mercury Séguin treated fine cinnabar with aqua regia and obtained, on the one hand, release of nitrous gas, and on other, oxidation of mercury and formation of sulfuric acid by combustion of sulfur. Analysis of the products indicated that the fine cinnabar was composed of 13.4228% of sulfur, and of 86.5772% of mercury (Séguin, 1814d).

Séguin confirmed his results with some additional experiments: (1) He now put in a small, curved retort, two parts of sulfur and one of mercury; and I dipped the curved part of the retort in a solution of lead acetate. Upon heating, sulfur and mercury combined and formed ethiop, but there was no precipitate in the solution of lead acetate, proof that no hydrogen sulfide was given off. He even continued the fire until the cinnabar was formed and had no more precipitate in the dissolution; (2) he mixed three parts of sulfur and one of mercury in a marble mortar, tightly covered with a cloth soaked in a solution of lead acetate. In the middle of this cloth was a small opening, which allowed the entry of the pestle, but not the communication of the outside air with the inside of the mortar. The mixture was triturated for three hours yielding very fine ethiops, but without evolution of hydrogen sulfide and without alteration of the color of the lead acetate; and (3) he ground a mixture of one part of molten sulfur and one part of mercury, in a mortar covered with a cloth soaked in lead acetate. Again, he obtained very fine ethiop, but without evolution of hydrogen sulfide. All these results, and additional experiments, proved conclusively that ethiop was a simple compound of sulfur and mercury without hydrogen and oxygen. In addition, they showed that ethiops prepared in the usual manner, contained sulfur in a very large proportion, greatly surpassing that of mercury; that in ethiop, made by the mixture of sulfur and cinnabar, sulfur was present in a lesser proportion than that of mercury; that in ethiop, which obtained by heating cinnabar slightly, contained even less a proportion of sulfur; and finally, that in ethiop made by a mixture of cinnabar and mercury, the proportion of sulfur was much smaller compared to that of mercury (Séguin, 1814d).

## *Rosin*

Séguin wrote that a good rosin was a very valuable substance for the musical arts because it contributed to the purity, the accuracy, and the strength of the sounds, which was drawn from stringed instruments (Séguin, 1814e). Unfortunately, the standard commercial rosin was far from enjoying these properties. If it was too greasy, it slipped on the cord; if it was too dry, it did not adhere sufficiently to it and required too frequent removal. The need for a rosin that satisfied these properties was clear. A quick examination of commercial rosin showed that it was constituted of resin and essential oil, and residues of turpentine and pitch. The resins were compounds of carbon and hydrogen united in such proportions that they quickly reformed new essential oil. The resin in the pure state was very friable and held a very short time on the bow. These defects could be eliminated by removing part of the constituent hydrogen; the resulting product was not friable, was more consistent, and could no longer form essential oil (Séguin, 1814e).

Séguin tried several physical and chemical procedures to remove the essential oils, among them, vaporization by gentle heat and treatment with acids (diluted sulfuric, acetic, HCl, etc.). These treatments removed the essential oils in different percentages and improved the quality of the remaining resin, but not enough. Eventually he found that dissolving the resin in alcohol and adding water resulted in the resin floating in the liquid while the essential oil remained suspended. Separating the upper layer and repeating the process several times largely reduced the essential oil. Ultimately, he discovered that replacing the alcohol by ether resulted in the total elimination of the essential oils (Séguin, 1814e).

The next stage was changing the ratio carbon/hydrogen, which made the resin friable. Again, Séguin tried several procedures to achieve this goal, among them, the slow action of heat and treatment with concentrated sulfuric. Finally, he found that the objective could be achieved treating the purified resin with nitric acid or with chlorine. The process with chlorine was more controllable and was selected (Séguin, 1814e).

The basic process was as follows: The commercial rosin was boiled for four to five hours in boiling water, with stirring. This operation eliminated a very large part of the essential oil. The residue was dissolved in a small quantity of alcohol and filtrated. The transparent liquor was treated with a stream of chlorine. The gas transformed first the alcohol into ethyl chloride, and then removed part of the hydrogen present in the resin, while destroying the remaining essential oil. The liquor was filtered and mixed with water and the floating resin separated by filtration, washed with water, neutralized with KOH, treated with acetic acid, and filtered again. The solid was washed with water to eliminate all the alkaline salts and then melted and poured into small paper molds. In this state, the rosin was very pure, transparent, slightly crumbly, forming a very fine and very dry powder under the fingers; enjoying all the properties appreciated by artists and the manufacturers of stringed instruments (Séguin, 1814e).

## *Coffee*

In 1814 Séguin published a long memoir (read to the Académie in 1816) about the chemical properties of coffee, roasted and unroasted (Séguin, 1814h).

Séguin mixed one part of unroasted coffee with four of distilled water and macerated it for several hours. The filtrate was a transparent brownish liquid, which turned dark green when boiled, while separating a large quantity of greenish gray flakes, which, after swimming in the liquor, precipitated. The precipitate was found to be an albuminous substance, which, behaved like egg white. The same result was obtained when carrying the experience in the absence of air. In another experiment, he extracted the unroasted coffee with alcohol of relative density 0.824 and cooled the resulting liquor to -6 ° C. This resulted in the separation of a large quantity of oil. Distillation of the residual alcoholic solution left a yellow liquid, which Séguin named bitter principle of alcohol. Water extraction of the new residue resulted in the separation of albuminous flakes that were found to be an intimate combination of albumin and bitter principle (Séguin, 1814h).

Further study of these four components, showed, for example, that the distillation of the albumin fraction gave a large amount of ammonia. This albumin was soluble in alkalis and reacted with nitric acid providing oxalic acid. Distillation of the bitter principle of coffee, also gave a great quantity of ammonia. The principle was more soluble in water than in alcohol, it was slightly acid, did not release $CO_2$ by exposure to oxygen, it was not precipitated by sulfuric acid, and with chlorine produced a precipitate only after contact of eight to ten days. It produced colored solutions or precipitates with several chemicals, for example, with potassium chromate, a brown solution, with ferric sulfate, an emerald solution, with mercuric chloride, a yellow-white precipitate, with tin chloride and lead acetate, a yellow precipitate, and with cupric acetate, a pistachio color precipitate (Séguin, 1814h).

The oil component was white as lard, odorless, and had a bland flavor. It did not burn with oxygen but eventually turned rancid. It was insoluble in cold and hot water and distilled over naked heat did not release ammonia. The aqueous solution of the green matter of coffee became cloudy, precipitated, acidified, and gave $CO_2$ on exposure to the open air. It precipitated abundantly by the addition of an acid, even acetic acid, at the rate of the albumin which it contained, proof that albumin had more affinity with acids than with the bitter principle. It was very soluble in water, but not in alcohol of relative density 0.824 (Séguin, 1814h).

Séguin also described the action of many reagents upon solutions of coffee in its various states (unroasted and roasted), among them, limewater, a solution of alum, acids, alcohol of relative density 0.824, gelatin, solution of tannin, atmospheric air, etc. These results showed that roasted induced in coffee marked changes. It destroyed part of the albumin, proportionately increased the quantity of the bitter principle, partly dehydrogenated this principle, and thereby increased its flavor. This degree of dehydrogenation should not be carried too far, because it would make the bitter principle to acquire an unpleasant bitterness (Séguin, 1814h).

Séguin concluded: (1) that the four components of coffee were present in different proportions according to the nature of the coffee, its degree of maturity, the soil which produced it, the time of its conservation, the care taken to preserve it, its degree of drought and the care taken in sorting its grains (2) that roasting, above all, changed all the proportions of these principles, and that it was necessary to destroy in large part the albumin, consequently the green matter, and to increase the relative proportion of the bitter principle and give it a new flavor; (3) that there was in roasting an intermediate degree where the coffee enjoyed its maximum quality, and that to obtain the best coffee, it was necessary to reach and not exceed this correct degree; (4) the albumin and the bitter principle contained a great deal of nitrogen, which reflected in the release of ammonia when the coffee was burnt in a retort or with naked fire; (5) that the solution of unroasted coffee became cloudy and putrefied by its exposure to the air at the rate of its albumin, which at first precipitated by coagulating and then putrefied in the manner of animal matters; and finally (6) that the dissolution of unroasted coffee produced an abundant precipitate with the dissolution of tannin, forming an albuminous tannate, while the dissolution of roasted coffee produced only a much weaker precipitate due to the destruction of the greater part of the albumin during roasting (Séguin, 1814h).

## *Alkaloids*

### Cinchona

Séguin treated with cinchona several members of his household affected by fever and noted very marked differences with the results. This fact led him to suspect the purity of the febrifuge principle that he had employed (Séguin, 1814g). His first work was devoted to identifying the true febrifuge principle of cinchona, of distinguishing the species, which contained it from those which did not; and lastly, to appreciate its quantity and quality. At this time, he was not interested in detail on the nature of the febrifuge principle, of its component parts, and of the results of its various actions on the system, either as a physical agent or as a chemical agent. Taste and visual aspect were the only indications of the presumable qualities of commercial cinchona. Superfluous and non-measurable properties such as bitterness and a resinous and very slightly stringy appearance, were signs of good quality. The situation was even more complicated by the fact that the bark came in different colors, depending on if it was collected in Peru, Santo Domingo, or St. Lucia, and if it was falsified or mixed cinchona. According to Séguin, the only possible invariable indicators seemed to be the reaction with known chemicals (Séguin, 1814g). His experiments on the subject indicated that a first indication of the abundance and quality of the active component present in a sample was its reaction with the solutions of tannin, gelatin, and ferrous sulfate. For example, if the sample did not precipitate the tannin solution, was proof enough that it did not contain the febrifuge principle; if it only precipitated the solutions of tannin and ferrous sulfate, it proved it contained an astringent and non-tanning substance, which was foreign to it. And finally, if it precipitated the solutions of tannin, ferrous sulfate, *and* gelatin, it was proof that it contained an astringent and tanning substance. The more the amount of precipitate, was a qualitative signal that the febrifuge principle was abundant and of good quality. Séguin submitted to this kind of analysis over six hundred samples of all the known species of cinchona, taken from all the apothecaries and druggists of Paris and Versailles and was not surprised to find that very few of them satisfied his criteria. Most of them were found to be deprived of any febrifuge principle, or mixed with foreign matter, or of a very inferior quality (Séguin, 1814g).

Séguin remarked that the best manner to conduct his test was to boil 4 g of crushed bark in 57 g of water for half an hour, followed by decantation and filtration. The febrifuge was known to be little soluble in cold water; cooked for a longer time resulted in decomposition of the principle and using too much water could obscure the dissolution of the tannin. A sample of the extract was mixed dropwise with the tannin solution until no more precipitate was formed. A good cinchona would form a precipitate from the first drop; if the cinchona were of second quality, it would do it only after several drops, if the cinchona were mediocre, the liquor would only become cloudy but without forming a precipitate; finally, if the cinchona were of poor quality, the liquor would not cloud, and no precipitate would form. Séguin also explained the manner to test the sample with gelatin, ferrous sulfate, and a mixture of the reagents (Séguin, 1814g).

The next set of experiments compared the quality of the febrifuge principle contained in cinchonas of different colors. The results indicated that there was little difference between the good cinchona of various species. Nevertheless, Séguin understood that factors such as the nature of the soil, the age of the tree, its exposure, the degree of maturity of the bark, the season in which it was grown and exploited, its transport and its conservation, etc., could result in different activities (Séguin, 1814g).

The second section of the memoir was devoted to the analysis of additional experimental results that complicated the interpretation of the previous results. He now found that both a distinct bark and the tanning principle were characteristic of the presence of febrifuge activity. Both were found in various substances in greater or less quantity, but often accompanied by principles, which contradicted their principal properties. This led him to classify the cinchonas commercially sold, in six very distinct classes, on the basis of their reaction with gelatin and the solutions of tannin and ferrous sulfate (Séguin, 1814g).

The first class included cinchona (sold as such) that did not precipitate gelatin or the tannin solution but formed with ferrous sulfate a precipitate soluble in acids and insoluble in alkalis, properties common to purely astringent substances. Séguin named this class *fake cinchona,* a material that was sold at very low prices. The second class included the cinchonas that did not precipitate the solutions of tan, of gallnut, of gelatin, and of ferrous sulfate. The corresponding barks had the external characteristic of cinchonas but were less bitter. The third class included the cinchonas that did not precipitate gelatin and ferrous sulfate and weakly precipitated the tannin solution. These contained a small amount of the febrifuge principle and hence acted only in large doses, which made them particularly dangerous for the possibility of ingesting dangerous materials. The fourth class of cinchonas included those which did not precipitate gelatin and ferrous sulfate, but which precipitated abundantly the solutions of gallnut and tannin. These cinchonas had good taste and appearance, and were very effective, as proved by experience. The fifth class of cinchonas included those which precipitated the solutions of tannin and ferrous sulfate but not gelatin. This cinchona was yellow and was sold under the name Angustura. The iron precipitate was ferruginous, yellow, abundant, and soluble in alkalis. The last class included the cinchonas, which precipitated gelatin and the tannin solution, but not ferrous sulfate. These cinchonas were very effective. According to Séguin, his results indicated the need to classify in an orderly manner all the cinchonas sold commercially. These barks sometimes contained common principles, and often quite different principles. Some were usefully employed in fevers, others in dysentery, others in the case of gangrene. It was therefore appropriate to classify them not only based on their external characteristics, but also based on their chemical properties (Séguin, 1814g).

## Opium

Séguin wrote that the substance called opium, which came from *Papaver somniferum,* was a product of clear medical importance. In spite that it had been extensively investigated, there was much contradiction in the results reported. This led Séguin to carry additional experiments trying to know better the nature of opium, to isolate all its principles, to determine the action of each of them on the animal economy, and to indicate with certainty, which were the substances which should only be administered, and which ones such be discarded (Séguin, 1814l).

The first step was washing with enough cold water, commercial opium crushed into small pieces. This action removed all the substances soluble in water, which constituted about 75% of the crude material. These two fractions were separate and analyzed separately (Séguin, 1814l).

The liquid phase was nauseous; its bad smell could be eliminated by continuous boiling. It was also very acid due to the presence of a small quantity of acetic acid. Séguin studied its reaction with a variety of reagents. For example, the alkalis and ammonia formed abundant precipitates, insoluble in water, but soluble in alcohol when hot. Upon cooling, the alcoholic extract precipitated whitish and prismatic crystals, which were purified by repeated dissolution and recrystallization from alcohol. The purified crystals were insoluble in cold and hot water, but soluble in hot aqueous alcohol. Séguin tested the action of several reagents upon the crystals. For example, they were soluble in acids, turning them bitter. Distilled over an open fire they decomposed yielding ammonium carbonate, an oily matter, and a charcoal, which did not contain any mineral compound. Finally, they did not form oxalic acid, when treated with nitric acid. Further treatments resulted in the separation of a vegetable acid, which colored red a solution of ferrous sulfate and formed with solutions of baryta, strontian, calcium, lead and tin, abundant precipitates. Séguin also separated two substances, one insoluble in water, dark grey and of bitter flavor, which he named the bitter and insoluble principle of opium; and a second, soluble in water, shiny, of rather pleasant odor, strongly bitter flavored, deliquescent, which did not yield oxalic acid when treated with nitric acid. Séguin named this second substance the bitter and soluble principle of opium (Séguin, 1814l).

According to Séguin, his results indicated that the aqueous phase of the extraction process contained at least five substances: (1) acetic acid; (2) a crystalline unidentified new substance; (3) a new acid, which had peculiar properties, probably acetic or malic acid, modified by some combination or by some other circumstance; (4) a bitter and insoluble principle of opium, insoluble in water, but soluble in alcohol, acids, and alkalis; and (5) a bitter and soluble principle of opium, soluble in water and alcohol (Séguin, 1814l).

The solid residue of the extraction process (marc of opium) was also subjected to a series of analysis to identify its components. Séguin described it as being like gluten, it softened when heated, taking on an oily appearance. The results of the chemical tests indicated the opium marc contained (1) a certain quantity of the crystalline substance of opium; (2) an oil; (3) a vegetable substance having an analogy with starch; (4) a small amount of unclean bitter principle; and (5) plant debris (Séguin, 1814l).

According to Séguin, the multiplicity of components explained why the products of opium had a such a variable action on the animal economy. He estimated that 100 parts of commercial opium contained, grossly, (1) pure crystalline plant substance, 4 parts; (2) an acid with special properties, 10 parts; (3) insoluble bitter, 12 parts; (4) soluble bitter, 20 parts; (5) oil, 20 parts; (6) starch-like substance, 10 parts; (7) acetic acid, 2 parts; (8) water, 10 parts; and (9) debris, 12 parts (Séguin, 1814l).

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