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# JEAN-FRANÇOIS BONASTRE

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**RESUMEN**. Jean-François Bonastre (1783-1856), un farmacéutico francés; dedicó la mayor parte de su vida al análisis y determinación de las propiedades de un gran número de substancias naturales, sus principios activos, y sus resinas. El trabajo que realizó sobre la resina styrax lo llevó a descubrir el estireno.

**ABSTRACT**. Jean-François Bonastre (1783-1856) a french pharmacist, devoted most of his efforts to the analysis and determination of the properties of a large number of natural substances, their active principle and their resin. His work about the styrax resin led him to discoverer styrene.

Jean-François Bonastre was a French pharmacist, member of the Société de Pharmacie de Paris since 1818, President of the same for 1844, resident member of the Société Linnéenne de Paris, and member of the Académie Royal de Médicine since 1824.

## **SCIENTIFIC CONTRIBUTION**

Bonastre published about 50 papers, mostly in the area of natural products, and within it, identification and analysis of their active principles. He also did some interesting work in the analysis of the mummification process carried on by the ancient Egyptians.

#### Resins

According to Bonastre, natural resins were substances composed of (1) a volatile oil, (2) an acid, (3) a resin proper, soluble in cold alcohol, (4) a sub-resin, almost always insoluble in boiling alcohol and ether, and (5) a bitter extract accompanied by some salts. Volatile oils were composed of hydrogen and carbon in an appropriate ratio and were capable of absorbing gases such as oxygen and nitrogen. With oxygen they produced acids in smaller or larger amount, depending on their age. Examples of this phenomenon were the volatile oils of clove, canella, sabine (extracted from *Juniperus Sabina*), brandy mint, etc., all of which reddened litmus paper. Absorption of nitrogen was a partial cause of the aroma they exhaled, produced by chemicals such as hydrogen cyanide, benzoin, and benzoic acid.

The acid was usually present in the fraction of the resin soluble in alcohol and its nature depended on the genre of the vegetable; benzoic acid was present in plants belonging to the *liquidambar* and styrax *genre*, while succinic acid appeared in resins of the genre *pinus*. Bonastre himself had found that the resin elemi (*Amyris elemifera*) contained a volatile acid, slightly soluble in alcohol, and crystallizing in thin small strips; he had also found an acid to be present in the resins liquid styrax, natural rubber, sandarac (*Tetraclinis articulata*), mastic, copal, gum anime, etc. The subresin was a substance without volatile oil, usually crystallizable, and having variable properties, dependent on the original resin. Thus in the balm of Mecca and in the resin elemi the sub-resin was white, spongy, lighter than water, able of supporting heat without decomposing, and generating an acid when contacted with nitric acid. The sub-resin present in the balsam of Canada was quite dry and friable, denser than that of elemi and insoluble in boiling alcohol. The sub-resin from the turpentine from Bordeaux dissolved when slightly heated, was soluble in aqueous alcohol, and could be prepared in a pulverulent form. The copal sub-resin was hard and rough, and almost insoluble in ether. Natural rubber contained the largest percentage (94 %) of sub-resin, among all the known resins. It was insoluble in boiling alcohol and swelled in the presence of cold ether while slightly dissolving.

Bonastre explained that the use of the term sub-resin was not to create a new word but to emphasize the two degrees of solubility present in the same substance. He had been asked if a sub-resin was not simply a pure resin lacking the acid and the volatile oil, while the soluble resins were the same resin in a raw state. He indicated that if the alcoholic solution of the resins of anime were united and filtered, they produced one liquid phase colored by two transparent shades, which became turbid when agitated and returned to be clear after being left alone. In this situation, there were two clear phases, separating both resins. This observation showed that the soluble resin, the sub-resin, the acid, and the volatile oil were reunited in the same vehicle (the alcohol), which kept all of them in the liquid state. Why then, agitation made it turbid and repose clarified and separated them? The two resins had to be of different nature otherwise they would be equally soluble. In the case of the *amyris* (a genus in the citrus family) the two resins were even more different. Another interesting result was that a sub-resin, deprived of its acid and volatile oil, seemed to be sublimable and some of them were phosphorescent. According to Bonastre, his results indicated that sub-resins had the following characteristics: (a) Were absolutely deprived of essential oil; (b) did not show an alkaline behavior even when deprived of their acid; (c) were only soluble in boiling alcohol, in ether, and in volatile oils; (d) were capable of assuming definite crystalline forms; (e) did not generate soapy material with caustic alkali, and (e) some were phosphorescent.<sup>2</sup>

In a following paper Bonastre reported that gum elemi, gum alouchi and the gum arbol-a-brea from Manila were phosphorescent when pounded in a porcelain mortar with a glass pestle. In gum elemi the light was pale and feeble and less than was observed in pounding sugar. In gum alouchi, well dried and heated, the light was much more vivid, the color a little reddish, and gave out slight scintillations. The gum arbol-a-brea was more luminous than sugar and even emitted light by friction in water. When these three gums were treated with dilute sulfuric acid, they showed the same degree of phosphorescence. His results indicated that the sub-resin of elemi was a white, extremely light substance; the one of alouchi appeared as silver white flakes, also very light; and the resin of the arbol-a-brea was extremely white and brilliant.<sup>3</sup>

In another publication Bonastre described the characteristics of the crystals of several sub-resins, among them caryophyllene (*Caryophyllus aromaticus*), ceroxyline (*Ceroxylon andicola*), elemi, arbol-a -brea, alouchi, etc.<sup>4</sup>

#### Styrene

In 1827 Bonastre communicated to Société de Pharmacie his observations on a crystalline deposit, which had been formed progressively during several years in an alcoholic solution of tolu, the black Peru balsam (*Myroxylum peruiferum*). These crystals were internally white and externally brown and covered by a layer of the balsam, had a slight acrid taste, were insoluble in cold and boiling water, and soluble in hot aqueous alcohol. The alcoholic solution was acid and on cooling deposited flakes, which had all the appearance of benzoic acid. Bonastre neutralized the solution with calcium carbonate, brought it to boiling an then the filtrate to cool spontaneously. Addition of HCl precipitated the benzoic acid not as beautiful crystals but as a white spongy crystalline mass.<sup>5</sup>

Some months afterwards he observed a similar crystallization in an alcoholic solution of liquid styrax (a gum exuded by the tree *Liquidambar styraciflua*). The yellow white crystals, shaped like needles, were insoluble in water and had a sweet non prickly taste. Their alcoholic solution was not acid and evaporated alone left a mixture of crystals and a sweet oily substance smelling like vainilla. The crystals were insoluble in cold and boiling water and did not react with quicklime, showing they were not benzoic acid but a resinous or balsamic sub-resinous crystallizable substance, which Bonastre named *styracine*. Bonastre believed styracine was present in liquid styrax, mixed but not combined with benzoic acid.<sup>5</sup>

In another short notice, Bonastre reported that the styrax or Storax of Bogota, which was being imported from South America as a replacement of ordinary styrax, contained benzoic acid, an odorant and very soluble resin, a small amount of a bitter extract, and wooden matter.<sup>6</sup>

According to Bonastre, chemists separated fluid resins and false balsams from true balsams on the fact that the first two did not contain benzoic acid while the third did it in substantial amounts. The separation between fluid resins and false balsams was rather tenuous; it was based on the difference of their smell, a rather elusive property. His experience had shown him that it was not necessarily true to admit the presence of free benzoic acid in all true balsams. The exams used for this purpose were not necessarily faultless. As an example, he mentioned the American sweet gum (Liquidambar styraciflua), originating from Mississippi and added that probably those of tolu, storax, and benzoin (originating from plants of the Styrax genre) also showed this problem. Very few of the true balsams had been analyzed in the dry state, and not in the fluid or fresh one. The fresh American sweet gum, obtained from incisions made in the tree, was also known as liquid amber because of its fluidity and particular yellow color. It had a transparent oleaginous aspect, a strong piquant smell similar to that of liquid styrax, an acrid and very aromatic taste; it froze at about 0 °C becoming non transparent, it was lighter than water, slightly soluble in alcohol yielding an acid solution, completely soluble in ether, and showed no reaction with oxygen. Treated with cold nitric acid it converted into a thick resin, which did not contain benzoic acid. The portion insoluble in alcohol remained mostly in a crystalline state and appeared to be similar to the one Bonastre had found in the tincture of liquid styrax and named it styracine. A chemical analysis indicated that the volatile oil contained 89.25 % carbon, 10.46 % hydrogen, and 0.0029 % oxygen. Bonastre believed that the oxygen originated from an external source.

Bonastre distilled 100 g this balsam in the presence of 1 000 g of water and obtained 7 g of white colorless volatile oil, lighter than water, having a penetrant odor and an acrid burning and disagreeable taste. Further distillation of the water used in the previous process yielded two fractions: The initial one was a very aromatic and strong tasting transparent liquid. The second fraction was a waxy odorless substance, containing a crystallizable matter. The liquid residue of the first distillation was slowly evaporated until it begun separating a large amount of benzoic acid.

After additional analysis of the different products of the distillations Bonastre concluded that American sweet gum contained a series of substances crystallizing at different temperatures, as well as non-crystallizable ones, such as oleoresin. On the basis of 100 g of original material, he found 7 g of a volatile colorless oil, crystallizing at 0 °C, 11.1 g of a semi-solid matter contained in the distilled water, and separated by ether, 1 g of benzoic acid, 5.3 g of crystalline matter soluble in water and alcohol, 2.05 g of a yellow coloring material, 49 g of oleoresin, and 24 g of styracine (for a total of 99.45 g). The analysis of the purified crystals of styracine indicated that it contained 76.2728 % carbon, 5.5032 % hydrogen, and 18.2240 % oxygen, that is, 2 % less oxygen than benzoic acid. To Bonastre this suggested it was a hypobenzoic acid or a benzoate of hydrogen bicarbonate.<sup>7</sup>

In 1831 Johan Eduard Simon claimed that the result found by Bonastre between liquid styrax and the commercial one was due only to its freshness and higher purity. He performed a large number of additional experiments in order to clarify the characteristics of liquid styrax. Among other things, he found that the acid it contained was not benzoic but cinnamic, and that the essential oil obtained by distilling liquid storax with water and sodium carbonate was limpid, had the very agreeable smell which was peculiar to storax, was soluble in alcohol and in ether, and refracted the luminous rays like creosote. After kept for some months it had thickened into a transparent, gelatinous mass and become insoluble in ether and alcohol. Simon suggested naming the volatile portion *styrol*; an elementary analysis indicated that it contained an equal number of atoms of carbon and hydrogen (92.46 % carbon and 7.54 % hydrogen), so it should be considered an isomer of benzene. The solid residue of the distillation was given the name *styrol oxide*. According to Simon, styracine contained 84.47 % carbon, 6.32 % hydrogen, and 9.21 % oxygen.<sup>8</sup>

The techniques available at that time did not allow Bonastre and Simon to realize they had separated the oxidation products of styrene and its polymers.

John Blyth and August Wilhelm Hofmann (1818-1892) did the following critical work in which they were able to isolate styrene. In the introduction to their paper they wrote "the early investigations of balsams were purely qualitative; everything crystalline and which united with bases was benzoic acid; those, on the other had, which did not enter into combination were described as camphor. If, on distillation, a volatile fluid was obtained, it was sufficient to state that the substance contained also a volatile oil.<sup>9</sup>

Blyth and Hofmann followed Simon procedure to prepare styrole: steam distillation of a mixture of liquid styrax with water and sodium carbonate, in a copper retort heated gently. The distillate consisted of a heavy layer of water surmounted by a slightly yellow layer of the oil. The latter was dried with fused calcium chloride and purified by distillation. Pure styrole was described as "a colorless transparent fluid of burning taste and peculiar aromatic odor...Exposed to a mixture of solid  $CO_2$  and ether it solidifies instantaneously in a white beautiful white crystalline mass." It boiled at 145.75 °C, and was completely soluble in ether and absolute alcohol, methanol, acetone, carbon disulfide, and ethereal oils. Elemental analysis indicated it contained two equivalents of carbon and one of hydrogen, corresponding to the formula  $C_{16}H_8$  (using C=75 and H=12.5). Blyth and Hofmann reported in detail the preparation of derivatives such as nitrostyrole, benzoic acid, nitrobenzoic acid, its reaction with chromic acid, sulfuric acid, bromine, chlorine, the influence of heat, etc. etc. 9

Marcellin Berthelot (1827-1907) carried on an extensive research project on the reactions of acetylene; within it he achieved the synthesis of styrene from benzene and ethylene, of naphthalene from styrene and ethylene, and of anthracene from benzene and styrene.<sup>10</sup>

An interesting fact is that the chemist Caspar Neumann (1683-1737) carried out the distillation of storax about 100 years before Bonastre. William Lewis (1708-1781), in his translation of the works of Neumann, writes: "out of an ounce of common Storax, rectified spirit of wine dissolved six drams. From the residuum, water extracted half a dram of gummy matter. The rest was almost mere sawdust. Another ounce of the same Storax treated with water at first, gave two drams of extract, after which it yielded with spirit four drams of resin, the saw-dust remaining as before". Antoine-François Fourcroy (1750-1809), 12 in his *Elements of Natural History and of Chemistry* 13 reported that "Neuman a fait l'analyse du storax calamite; il en a retire très peu d'huile essentielle, un sel acide concret, une huile épaisse" (Neuman has analyzed the storax calamite and separated a very small amount of essential oil, a concrete acid salt, and a thick oil). The *Dispensatory of the United States of America* 4 added: "Neuman obtained from 480 grains (31.10 g) of storax 120 (7.78 g) of watery extract; and from an equal quantity 360 grains (23.33 g) of alcoholic extract. It yields benzoic acid by distillation, and is therefore entitled to the rank of a balsam. It contains also resin and a volatile oil".

## Ancient plants and fruits

In a paper published in 1828 Bonastre reported that the philologist Jean-François Champollion (1790-1832) had sent him for analysis a large number of fruits and other part of vegetables the ancient Egyptians had deposited in the sarcophagi of their mummies and in underground tombs. The purpose was to determine up to what point chemistry could help in determining the nature of vegetable substances recovered after many centuries of being without contact

with external factors. Although some of them were somewhat altered in their physical qualities, it was found that most of their immediate principles had been able to keep their principal chemical properties, which together with their botanical characters, could help in recognizing their identity.<sup>14</sup>

In this publication, Bonastre reported the results for 19 different substances, among them, wheat (*Triticum hybernum*), pomegranate (*Punica granatum*), desert date (*Balanites ægyptiaca*), bread, flour from delphinium (*Delphinium ajacis*), citron (*Citrus medica*), areca (*Areca passa l'acqua*), a pine cone (*Pinus pinea*), a water chestnut (*Trapa natans*), black raisins (*Vitis vinifera*), lotus (*Rhamnus lotus*), doum palm fruit (*Cucifera thebaica*), Arabic gum, a black substance recovered from the inside of a mummy, etc. etc. Thus, the wheat grains, the bread, the flour from delphinium, the starch of the water chestnut and of the pine cone, macerated in boiling water, developed a strong blue color in contact with iodine tincture. The juice of the macerated pomegranate and of the areca, prepared with boiling water, did not react with the iodine tincture but gave an abundant black precipitate with ferric oxide. The fruit of citron, macerated in cold water, produced a very acid juice, which reddened litmus, and in contact with calcium carbonate generated an abundant stream of CO<sub>2</sub>. The chemical and physical properties of the black substance showed that it was asphalt (bitumen of Judea). According to Bonastre, all these results proved that immediate principles such as soluble gums, starch, resins, sub-resins, fatty acids, citric, tartaric, and gallic acids, tannin and other coloring substances, were able to remain intact after many centuries of existence.<sup>14</sup>

The confusion between the terms canella and cinnamomon, as reported by the ancient historians, was discussed and clarified in another paper. Bonastre stated the embalming material used by the Egyptians was cinnamomon and not canella as translated by Herodotus (484-425 BCE) and Diodorus of Sicily.<sup>15</sup>

In another publication Bonastre described the art symbols by which the ancient Egyptians had represented certain plants and fruits in monuments, sarcophagi, and underground tombs. He referred in detail to three plants: true lotus, and two kinds of papyrus.<sup>16</sup>

Bonastre also reported his inspection of two samples of balsam of Mecca, one rather fresh, and the other originating from the Egyptian Museum in Paris. This balm was extremely rare and consequently had been replaced in the commerce by the balsam of Canada (also known of balsam of Gilead). In his first publication, Bonastre showed the latter balsam was significantly different from the one from Mecca. These differences were very clear when both balsams were macerated with alcohol: The soluble and insoluble resins of the balsam of Mecca were soft and viscous, respectively, while those of the balsam of Canada were solid and fragile and pulverulent, respectively.<sup>17</sup>

The ancient sample was composed mainly of two substances, one fluid and transparent, the other hard and opaque. In addition, small crystalline masses were seen dispersed all over the balsam. The fluid portion was almost odorless and very soluble in alcohol; subject to steam distillation did not show the presence of a volatile oil. The aqueous fraction that passed over was found to contain acetic acid. The small amount of the sample available did not allow Bonastre to make a more detailed examination; he only remarked that the balsam of Mecca, after being stored for a long time, decomposed producing acetic acid and a crystalline matter. <sup>18</sup>

### **Analysis of mummy parts**

In 1833 the Académie Royale de Médecine requested from Félix Henri Boudet (1806-1878), Antoine François Boutron-Charlard (1796-1879), and Bonastre to analyze three substances originating from an Egyptian mummy: a portion of muscular flesh, a crystalline mass formed upon it, and a compound powder used by the Egyptians in embalming.<sup>19</sup>

The initial section of their report described the art of embalming as practiced by many people in Asia and Africa, particularly the Egyptians, as a sign of respect for their dead. The ancient Greek historians had described in a rather precise manner the procedures utilized for rich people, less rich, and the poor. For example, in the case of a rich person, the brain and the intestines were removed first, washed in wine and then thrown ceremoniously into the Nile. Then, the empty head and belly were packed with cedar gum, myrrh, cinnamon, and other perfumes, the whole body covered with a mixture of sodium carbonate and chloride, and after two months it was wrapped around with a strip of cotton or linen plastered with gum, ready to be put in the casket. In the case of less rich people, a liquid capable of dissolving the viscera was injected in the belly from the back and after some time removed by the same mean. The body was then covered with the sodium salts for 66 days, or returned to their relatives. In the case of poor people, the body was injected with a liquid called *surmaïa*, afterwards salted and returned to their relatives. Most of the substances used in the process were a trade secret of the embalmers, although it was believed some of them were Arabic gum and cedar resin. It was not clear if the liquid known as *surmaïa*, was acid or alkaline, or simply a particular mixture.<sup>19</sup>

The sample of muscular flesh belonged to the upper part of the thigh; it was covered with bandages and had a strong smell. The fleshy muscular layers, clearly perceived, were covered with a white, pearly crystalline deposit. This crystalline matter, formed by small needles, was odorless and tasteless; it fused at 59 °C; was insoluble in cold distilled water and sparingly soluble in boiling water and the solution did not react with litmus. It was partly soluble in boiling alcohol and the alcoholic solution reddened litmus. The crystals were treated with a variety of chemicals and the results indicated that it was a fat, which had all the properties of human margaric acid (probably a mixture of stearic and palmitic acids).<sup>19</sup>

The next section described the results of the examination of the dark yellow pulverulent material used in the embalming process and found in the mouth of the mummy. On exposure to dry air it was seen to be composed of several substances, easily separable by mechanic means: a balsamic substance, apparently wood flour storax (an impure form of styrax), although its properties were not so prominent to give a definite answer; a resinous material composed of small friable semi-transparent fragments, burning with a brilliant light and releasing a pleasant smell. Its behavior with alcohol, water, and alkaline bicarbonates suggested it was cedar resin; a gum resin, present as very small transparent yellow particles, of glassy aspect, and having a bitter taste different from the resin described above; its behavior with cold alcohol, ether, water, etc., suggested that it was myrrh; and a vegetable substance (fragments of fruits), presenting all the external properties of nutmeg (Bonastre believed this substance was mixed with the cinnamon of the ancients).<sup>19</sup>

The pulverulent material was calcined in a platinum crucible and the cinder found to contain sodium chloride.

According to Baudet, Boutron-Charlard, and Bonastre, their results indicated the embalming powder contained 40 % of soluble resins and sub-resins, 13.3 % of fatty material (butyric and stearic), 26.7 % gums, 13.3 % of wood residues, and 6.7 % of saline material composed of sodium chloride and calcium carbonate. 19

The report included an interesting footnote regarding the nature of the cinnamon of the ancients: "Within the fragments of fruits it was easy to recognize *cinnamomum* if by this term we were to understand canella; but Herodotus was perfectly well acquainted with canella; he designated it, not by the name  $\chi \iota \nu \nu \alpha \mu \omega \mu \nu$ , a word he never made use of, but by the term  $\chi \alpha \rho \phi \eta$ , which means small, dry, slender branches; and the Arabs at this very day call canella *kerfe or qerfeh*. Thus for about 2250 years, canella was known in Egypt under the name of  $\chi \alpha \rho \phi \eta$ . What can it then be but cinnamon? The ancients thought that the  $\chi \iota \nu \nu \alpha \mu \omega \mu \nu$ , originated from those places where Bacchus was brought up, and that this name was given to it by the Phoenicians who received it from the Arabs. Now Bacchus' country is India, with which the Arabs communicated by means of the Red Sea. Desfontaine believes that it is not possible to know the country from where cinnamon was drawn, and that we cannot know to what tree the cinnamon belongs. Some authors think it to be the canella bush. Sprengel thinks it is our *Laurus cinnamomum*. Stackhouse, on the contrary, considers that is *Laurus Cassia*. One of us, according to this analysis, which is in part confirmatory of the narrative given by the historians of antiquity, thinks that there is a large probability to see in the fragments of fruits resembling nutmeg the real cinnamon of the ancients". 19

#### **Natural products**

## Clove

Bonastre was led to investigate the properties of volatile oils by the researches of Michel Eugène Chevreul (1786-1889) on fatty materials and his general considerations about organic analysis. In the first stage he chose to study the compounds obtained by the reaction of the essential oil of clove (obtained by steam distillation) with alkalis and the oxides of barium, strontium, calcium, magnesium, and lead (PbO). This oil was transparent, colorless, had an acrid piquant taste, a density of 1.061, and was slightly soluble in water and very soluble in alcohol, ether, concentrated acetic acid, and fatty oils. It boiled below 100 °C, did not react with litmus paper, and nitric acid converted it into oxalic acid.<sup>20</sup>

When mixed with equal parts of caustic soda it hardened immediately and became opaque. The mixture was then diluted with water and distilled. The water that passed was covered with a layer of volatile oil different from the original one because it did not have the odor of clove and had a different density. The residue turned into a crystalline mass, semi transparent, and carpeted with numerous white brilliant needles; the water was eliminated by filtering between absorbing paper, followed by drying in a stove. It was now formed by silky fibers, white and brilliant, having the acrid and piquant flavor of clove, being totally soluble in hot water yielding an alkaline solution. Bonastre treated it with a variety of reagents and reported that with ferrous sulfate it turned lilac, with ferric sulfate it was initially red and finally blue, and with ferric malate it became brown. A chemical analysis (by calcination) indicated it contained 18.57 % of soda. The reaction with KOH was somewhat similar, except that the resulting soapy material (Bonastre named it *savonnule*) crystallized as silver white brilliant scales, which treated with nitric acid developed a beautiful red color. Chemical analysis indicated it contained 11.69 % of KOH. Mixed with aqueous ammonia, the essence of clove darkened somewhat and become granular in appearance. When exposed to air, the ammonia disappeared and the original oil reappeared. The savonnules prepared with the oxides of barium, strontium, and calcium was very similar, except for the form of the crystals formed. The savonnule with magnesium was very solid but non-crystallizable.<sup>20</sup>

All the above information was repeated with more details in another publication, which included also similar reactions with the essence of allspice, Jamaica pepper, *Myrtus pimenta* (the latter formed similar savonnules).<sup>21</sup>

Bonastre concluded that (a) the volatile oils of clove and allspice formed with alkalis and metallic oxides a very intimate union, which was less volatile in air or under steam distillation, (b) this combination did not turn red in contact with nitric acid and did not become oxalic acid under the action of heat; (c) nevertheless, these oils retained the acrid piquant flavor and the density of the original material; (d) under the influence of a boiling alkaline solution, they turned aqueous solutions of ferric oxide, red, brown, dark lilac, blue, or violet; (e) the volatile clove oil joined with base without changing its chemical composition; (f) these combinations seemed to occur in definite proportions but with excess of alkali. In this respect they seemed to be closer to the resinous soaps than to soaps of fatty materials;

and (g) the crystalline soapy materials of clove oil were clearly different from the white solid crystalline substance (which he named *caryophyllene*), which he had extracted with alcohol from the cloves.<sup>21</sup>

In a later publication Bonastre described a new crystalline substance he had extracted from the clove with water, after a long period of time of contact. It crystallized as thin silky transparent strips, completely soluble in alcohol and ether, which turned red in contact with cold nitric acid. Bonastre suggested naming it *eugenin*, to distinguish it from caryophyllene, the other crystalline substance he had separated from clove. He remarked that Jean-Baptiste André Dumas (1800-1884) had carried on an elementary analysis of eugenin and found its composition corresponded that of oil of clove minus one molecule of water.<sup>22</sup>

#### Laurel berries

According to Bonastre, the vegetables that composed the laurel family had provided medicine with a wide variety of useful substances. These had been obtained from all the parts of the bush, the roots, trunk, bark, leaves, and seeds. Bonastre was particularly interested in studying the berries of laurel and compare the results with those known for nutmeg. In the initial stage, he repeatedly macerated 100 g of peeled berries in 1 000 g of absolute alcohol at room temperature, filtrated the dissolution, and concentrated the filtrate by evaporation. He then observed that the liquid had split into two phases, the upper one a green liquid and the lower one slightly alcoholic and lightly turbid. In both phases there appeared crystals shaped as white transparent needles, having a bitter and acrid taste and an odor weaker than that of laurel. They were insoluble in cold water, slightly soluble in boiling water and cold alcohol, totally soluble in boiling alcohol and in ether. Deprived of the oil that accompanied them, they turned orange red in contact with sulfuric acid and were not altered by nitric acid or by alkalis.<sup>23</sup>

The oil of laurel was green and very bitter and in this aspect resembled fatty oils, but differed in being completely soluble in cold alcohol and in ether. It formed soft soaps with NaOH and KOH and an almost liquid soap with ammonia. The residue remaining from the cold alcohol maceration was treated with boiling alcohol, followed by filtration. On cooling, the filtrate deposited a fatty white material, which proved to be stearin (meaning a solid fat). This stearin was composed of two substances, limpid oil, which became rancid after a few days, and a solid substance like wax, which did not become rancid.<sup>23</sup>

A steam distillation of the peeled berries yielded an aromatic liquid mixed with a small amount of essential oil. The latter solidified into a white substance, extremely bitter. The distillation was very slow because the berries contained a large amount of mucilage, starch, and fatty substances, which obstructed the vaporization of the liquid. Further examinations led to the conclusion the laurel berries contained (besides water) a volatile oil, a crystalline matter (which Bonastre named *laurine*), green fatty oil, stearin, highly aromatic bark, resin, starch, an acid, and a noncrystallizable sugar.<sup>23</sup>

#### Pechurim

According to Bonastre, the beans of pechurim (*Ocotea pichurim*) were the fruit of a South America tree of the species of the Laurus, growing along the streams that flowed into the Orinoco. Two types of beans were available in the commerce, the large beans were commonly called sassafras nuts, because when grated they smelled like sassafras; the small beans smelled like pepper and had a more rounded shape than the large variety. These beans were locally used to treat dysentery and dyspepsia.<sup>24</sup>

Bonastre steam distilled the beans and noted that the passing liquid was covered with a supernatant layer of a white acrid bitter volatile oil, which browned a little in contact with air. This oil seemed to be composed of two different substances, one more odorant and volatile and totally soluble in alcohol, the other less odorant and volatile, and insoluble in cold alcohol. The reddish residue of the distillation was thick, mucilaginous, and highly bitter. It turned blue in contact with iodine proving it contained starch. Further tests indicated the starch was combined with gum and a coloring substance, and that the residue also contained stearin (solid fatty material). The grated beans when treated with cold alcohol and concentrated by distillation, separated into viscous oil and a dark colored glutinous substance. The latter was a resin very similar to the one of laurel beans and having a strong disagreeable odor. Additional testing showed the presence of tannin and a non-crystallizable sugar. The latter, treated with boiling nitric acid, yielded oxalic acid. Analysis of the cinders of the bean proved the presence of calcium oxalate. According to Bonastre, his analytical results indicated the beans of pechurim contained 3 % of solid volatile oil, 10 % of a butyric volatile oil, 22 % of stearin, 3 % of resin, 8 % of coloring matter, 11 % of starch, 12 % of soluble gum, 1.2 % of gum similar to tragacanth, 0.4 % of acid, 0.8 % of non-crystallizable sugar, 20 % of parenchyma, 6 % of water, and 1.5 of a saline residue.<sup>24</sup>

## Jamaica pepper (Myrtus pimento)

It was known that the berries of this tree, native of the West Indies, were collected and dried before they were ripe. In this state they were wrinkled, a little larger than the grains of black pepper, globular or oblong, and of a deepbrown color; they had an odor and taste, which seemed to be a mixture of that of pepper, cinnamon, and cloves. In 1825 Bonastre reported the analysis of the skin and the kernel of the fruit.<sup>25</sup>

In the first set of experiments, repeated macerations of the full berries with alcohol showed the appearance of a white flocculent matter, which settled on the bottom of the flask. The same result was observed when the crushed

berries were extracted with hot alcohol. The extracts had a very piquant taste and reddened litmus paper. Evaporation of the extracts, followed by cooling, showed precipitation of a green acrid, hot and piquant substance, a red extremely piquant matter, and a coloring extract covered with a brown layer. These results, which indicated the presence of two very different substances, in properties and amounts, led Bonastre to analyze separately the skin and the kernel of the berry.<sup>25</sup>

The shells were extracted with alcohol; the filtered infusion was yellow green and extremely piquant; it reddened litmus and turned brown green in the presence of ferric sulfate. Left to evaporate spontaneously it deposited a white substance joined with an oily green matter, heavier than water and having an ardent, acrid, and very piquant taste. This material was very soluble in alcohol and in ether. The husks, after being exhausted by alcohol, were seen to swell considerably when put into ammonia; the alkali dissolved a brown matter, which precipitated in brown flocks. The shells were also extracted with ether, steam distilled, etc., and the different fractions treated with iodine tincture, ferric sulfate, lead sub-acetate, gelatin, tin chloride, etc. Bonastre employed the same procedures to study the kernel of the seeds, with the following results:<sup>25</sup>

	Shells	Kernels
Volatile oil (heavier than water)	10.0	5.0
Green oil	8.0	2.5
Flocculent matter	0.9	1.2
Tannin extract	11.4	39.8
Gum united with tannin	3.0	7.2
Coloring matter	4.0	8.8
Resinous matter	1.2	3.2
Sugar matter	3.0	8.0
Malic and gallic acids	0.6	1.6
Ligneous matter	50.0	16.0
Ashes (salts)	2.8	1.9
Moisture	3.5	3.0
Loss	1.7	1.8

## Miscellaneous

In 1822 Bonastre analyzed a sample of *elemi* resin originating from *Amyris elemifera*, a plant from the citrus family, and found that it contained 60 % of a clear resin (separated from the resin by distillation), soluble in cold alcohol, 24 % of an opaque white resin substance soluble in boiling alcohol, 12 % of volatile oil, 3 % of a bitter extract, and 1 % of impurities.<sup>26</sup>

Bonastre also analyzed de resin of *alouchi*, obtained from a tree growing in Madagascar, the African coast, and India, and found it contained a soluble resin, a sub-resin, volatile oil, a bitter extract, an ammonia salt, and acid.<sup>27</sup> The publication led to a strong argument with Pierre-Joseph Pelletier (1788-1842) regarding the concept of organic alkalis.<sup>28,29</sup> This paper was followed by another one reporting that the capsules of sandbox tree (*Hura crepitans*) contained 51.1 % of a slightly acid fatty oil, 4.4 % stearin (solid fat), 38.9 % of albuminous parenchyma, 1.1 % gum, 2.2 % water, and 2.2 % of saline residue.<sup>30</sup> Among other plants analyzed were the balm of *Hedwigia balsamifera*),<sup>31</sup> a new species of myrrh,<sup>32</sup> the bark of massoy (*Massoia aromatica*),<sup>33</sup> the grains of musk seeds (*Abelmoschus moschatus*),<sup>34</sup> and the volatile oil of the cedar of Virginia (Juniperus virginiana).<sup>35</sup>

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