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SEBASTIANO DE LUCA Alkenes, glycerin, and derivatives, plant principles

SEBASTIANO DE LUCA Alquenos, glicerina y derivados, principios vegetales.

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ABSTRACT:

Sebastiano de Luca (1820-1880) was a multifaceted Italian-French chemist who carried on research on a wide variety of subjects, among them, the synthesis of numerous organic derivatives of iodine, the action of halogens upon glycerin, the separation of active vegetable principles, analytic, inorganic, physiological and atmospheric chemistry, formation of sugar in the liver and of oil in olives, as well as the analysis of the products derived from volcanic activity and of materials found in the ruins of Pompeii. He synthesized for the first time allyl iodide and pure propylene by the reaction between glycerin and phosphorus triiodide, and a large number of allyl derivatives (i.e. allyl ethyl, allyl phenyl allyl halides, allyl alcohol), and determined their physical and chemical properties. He also studied the action of phosphorus chlorides and bromides upon glycerin and synthesized the different epichlorohydrins and epibromohydrins. De Luca determined the composition of the tubercles of cyclamen and separated its active principle (cyclamin), the essence and composition of pear lemon, sweet maudlin, stigmaphyllon jatræphælium, and together with Berthelot synthesized artificial mustard oil and studied hepatic sugar.

KEYWORDS: allyl derivatives, cyclamen, epichlorohydrin, mustard oil, propylene.

RESUMEN:

Sebastiano de Luca (1820-1880) fue un multifacético químico italiano-francés que realizó investigación en una amplia variedad de temas, entre ellos, la síntesis de numerosos derivados orgánicos del yodo, la acción de los halógenos sobre la glicerina, la separación de principios vegetales activos, temas en química analítica, mineral, fisiológica y de la atmósfera, formación de azúcar en el hígado, formación del aceite en la oliva, así como el análisis de los productos originados por actividad volcánica y de los restos presentes en las ruinas de Pompeya. Sintetizó por primera vez el yoduro de alilo y propileno puro por la reacción entre glicerina y el triyoduro de fósforo, y un gran número de derivados alílicos (i.e. etil alilo, fenil alilo, haluros de alilo, alcohol alílico), y determinó sus propiedades físicas y químicas. También estudió la acción de los cloruros y yoduros de fósforo sobre la glicerina y sintetizó la diferentes epiclorhidrinas y epibromohidrinas. De Luca determinó la composición de los tubérculos del ciclamen y separó su principio activo (ciclamina), la esencia y la composición de la pera limón, la dulce sensiblera, el stigmaphyllon jatræphælium, y, junto con Berthelot, sintetizó la mostaza artificial y estudió el azúcar hepático.

PALABRAS CLAVE: ciclamen, derivados alílicos, epiclorhidrina, mostaza artificial.

INTRODUCTION**LIFE AND CAREER (COVELLO, 1862; NICOLAUS, 1890)**

Sebastian de Luca was born on November 4, 1820 in Cardinal (province of Catanzaro, Italy), one of the nine children of Martin de Luca, a pharmacist, and Mary Carello. His brothers and sisters were Eugenio Nicola Luigi Maria, Giovanna Rosa Giuseppa, Vincenzo, Elisabetta Maria Isabella, Francesco, Caterina Maria, Domenico Alfonso Sebastiano, and Giuseppe Maria. He received his basic education in Catanzaro and then moved to Naples to study natural sciences and chemistry (1838-1842); during this period he attended the

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private chemistry courses given by Raffaele Piria (1813-1865), the famous professor of chemistry at the University of Pisa and the leading Italian chemist of the day, known for his work on salicin (Covello, 1862; Nicolaus, 1890).

After graduation, de Luca returned to Calabria and took an active part in the failed 1848 revolt of the Italian states for independence from Austria. As a consequence he was sentenced to 25 years in prison. He was fortunate to escape arrest and board a French steamer, which took him to Marseille. Once in Paris he joined other Italian refugees and took advantage of this chemistry degree to become friend with the most important French chemists, such as François Arago (1785-1853), then secretary of the Institut de France (the former French Académie des Sciences), Antoine-Jérôme Balard (1802-1876), the discoverer of bromine, Jean-Baptiste André Dumas (1800-1884), Théophile-Jules Pelouze (1807-1867), and Marcelin Berthelot (1827-1907), with whom he would publish his papers about propylene, glycerol esters, and allyl chemistry, and help him develop a successful academic and research career (Covello, 1862; Nicolaus, 1890).

In 1857, at the recommendation of Piria, he was appointed to the chair of chemistry at the University of Pisa [succeeding Cesare Bertagnini (1827-1857)], where he also taught agricultural chemistry. He kept these positions until 1862 when he moved to the University of Naples to become the first full professor of chemistry. One of his first activities in Naples was the creation of the *Istituto Chimico*, structured according the French model (Covello, 1862; Nicolaus, 1890).

Sebastian de Luca passed away in Naples, on April 17, 1880, shortly after being appointed senator of the Kingdom for the 18th category, during the XIII legislature.

De Luca was ordinary member of the Società Reale di Napoli (1861), member of the Reale Accademia delle Scienze Fisiche e Matematiche di Napoli (1862), corresponding member of the Istituto Lombardo di Scienze e lettere di Milano (1865), director of the chemistry cabinet of the Scuola d'Applicazione per gli Ingegneri di Napoli and of Ateneo Italiano of Paris. He was appointed Knight of the Order of Saints Maurizio and Lazzaro, Officer of the Order of the Crown of Italy, and Commander of the Order of the Rose (Brazil). He served as mayor of the Municipality of Cardinale (Catanzaro) and official of the registry Antonio Rotiroti. In his position as secretary of the journal *Il Nuovo Cimento*, he was the addressee of the famous letter of Stanislaw Cannizzaro entitled *Sunto di un corso de filosofia chimica fatto nella Regia Università di Genova*, published in *Nuovo Cimento* 7, 321-366, 1858, widely publicized in 1860 at the Karlsruhe Conference, and leading to a clear understanding of the concepts of atom, molecule, and equivalent weight, and to the acceptance of Avogadro's hypothesis (Covello, 1862; Nicolaus, 1890).

SCIENTIFIC CONTRIBUTION

De Lucas published about 200 papers, booklets, and books (e.g., de Luca, 1865, 1874, 1879c) mostly in the areas of halogen chemistry, organic chemistry, inorganic chemistry, agricultural chemistry, and chemistry of natural substances. His book *Elements of Industrial Chemistry*. (de Luca, 1865) was based on the French edition of the *Dictionnaire de Chimie Industrielle*. In addition to the few publications described below, he also designed a more accurate apparatus for the dosage of CO. (de Lucas, 1853a) and a blowpipe with continuous jet (de Lucas, 1854c); he studied the production of nitric acid (de Lucas, 1855, 1856); the nature of water in an spheroidal state (de Lucas, 1860a, 1861a); iron prepared by hydrogen reduction (de Lucas, 1860e, 1861b); the formation of fatty matter in olives (de Lucas, 1861d, 1862a, 1863b) and the decomposition of guncotton (de Lucas, 1861c, 1864); he tested the action of hashish on himself, describing in detail its effects (de Lucas, 1862b) and researched the transformation of the skin of snakes into sugar (de Luca, 1863a); he did chemical research on the volcanoes Solfatara and Pozzuoli and the island of Vulcano, (de Lucas, 1863c, 1869, 1874) and carried on the analysis of diverse objects excavated from the ruins of Pompeii (de Lucas, 1879a b); etc.

IODINE

In 1853 de Luca was asked to analyze the possible presence of iodine in two samples of bromine originating from the Tissier factory. For this purpose he used the very simple and extremely sensitive procedure suggested by Antoine-Jerôme Balard (1802-1876), capable of detecting iodine even in the presence of chlorine and bromine (de Luca, 1853b). In this procedure the sample was introduced into a tube closed at one end, a few drops of carbon disulfide or chloroform added, and then a very dilute aqueous solution of bromine. The bromine decomposed only the iodides, without affecting the chlorides or bromides. Upon shaking the contents, the iodine dissolved in the carbon disulfide, tinting it a violet more or less, or a rose color when it was much diluted. This simple procedure allowed detecting the iodine contained in 0.01 of one mg of potassium iodide, and perhaps even smaller quantities. De Luca remarked the need not to use an excess of bromine, to avoid the formation of iodine bromide, which would not color violet carbon disulfide. If the solution tested was alkaline it was necessary to neutralize it with nitric acid, previous to treating it as indicated above.

The procedure also allowed quantification of the iodine. For this purpose it was necessary to prepare a standard solution containing one gram of bromine in four liters of distilled water. Dropwise addition of a certain amount of the standard solution released the corresponding amount of iodine; carbon sulfide was now added, removed, and replaced by a fresh identical quantity. The process was continued until the carbon disulfide did not change color (de Luca, 1853b).

According to de Luca this procedure was easily extended to mixtures containing chlorides, bromides, and iodides, as follows: (1) The total amount of the three halides was determined by their precipitation as silver chloride; (2) the amount of iodine determined by means of bromine, and (3) the combined amount of bromine and chlorine by means of a freshly prepared standard aqueous solution of chlorine (de Luca, 1853b).

In a following papers de Luca proposed several alternatives to the above process, using instead reagents such as silver nitrate and ammonia, cupric sulfate and SO_2 , manganese dioxide and sulfuric acid, hydrogen peroxide, and palladium salts and HCl , as well as the procedures to be followed to assure than none of these chemical contained iodine. He also reported that his experiments indicated that the atmosphere and rainwater did not contain iodine (de Luca, 1854a b). In additional papers he reiterated his claim that the atmosphere, rainwater, and snow did not contain iodine (de Luca, 1858a, 1859a, 1860b).

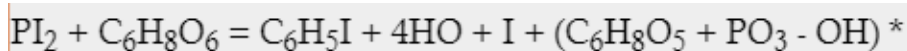
In 1859 de Luca reported that bromine could also be used to determine iodine by the dry way (de Luca, 1859b). In this case dry neutral potassium or silver iodide was placed at the bottom of a glass tube closed at one end and then a small glass bubble, closed at the two extremities and containing bromine vapors, introduced smoothly into the same tube. The air of the tube was replaced by dry CO_2 and the tube hermetically sealed using an alcohol lamp. By shaking the tube a few times the glass bubble was broken and the tube became full of bromine vapors, which decomposed the iodine in the form of violet fumes, which condensed on the cold part of the tube. The tube was now broken under water to assure the complete absorption of the gas. This simple procedure could be easily used to determine the presence of iodine in rainwater, and other waters. For this purpose the water was precipitated with silver nitrate, the precipitate washed and dried, and then treated with bromine in a closed tube. Any chloride or bromide, which could be present were not decomposed by the bromine, which acted only on the iodide, setting free iodine.

De Luca reported that he had used his procedure for the quantitative determination of iodine, by the repeated action of small weighed quantities of bromine upon silver iodide, until no more violet vapors were produced, or when the yellowish-red vapor of bromine made its appearance. The quantity of bromine used gave, by calculation, the quantity of iodine set free; this result could be checked by dissolving the liberated iodine in alcohol and testing it by a normal solution of SO_2 , and finally by converting the hydrogen iodide formed into silver iodide and determining the weight of the latter (de Luca, 1859b).

ACTION OF PHOSPHORUS TRIIODIDE UPON GLYCERIN

In 1854 Berthelot and de Luca reported the first synthesis of iodized propylene (allyl iodide) and opened a new chapter in organic chemistry. They found that when one part of crystallized phosphorus iodide (triiodide) and one part of concentrated glycerin were mixed together in a retort, a very energetic reaction took place; propylene gas was evolved, two liquids distilled over, and a portion of the matter remained in the retort. The two liquid phases were found to be water and allyl iodide, C.H.I (Berthelot and de Luca wrote C.H.I) and the residue a mixture of non-decomposed glycerin, iodine, a small amount of an iodized organic substance, phosphorus oxoacids, and a trace of red phosphorus. The proportion of the different products varied according to the relative amounts of phosphorus iodide and glycerin employed. For example, reacting one equivalent of phosphorus iodide with variable weights of glycerin resulted in the formation of one equivalent of iodized propylene and four of water (Berthelot & de Luca, 1854).

Berthelot and de Luca believed that their results indicated that the reaction was



Where the parenthesis represented the oxoacids of phosphorus mixed and combined with the excess of glycerin. This glycerin could be recovered by treating the mixture with lead oxide. According to this equation the production of allyl iodide equation was the result of the reductive action exerted by phosphorus iodide upon the oxygen of the glycerin (Berthelot & de Luca, 1854, 1855b). Berthelot and de Luca prepared phosphorus triiodide using Corenwinder's method (Corenwinder, 1850; Berthelot & de Luca, 1854).

Berthelot and de Luca determined the physical and chemical properties of allyl iodide and propylene and reported as follows:

(1) *Allyl iodide*, $\text{C}_3\text{H}_5\text{I}$, formed most of the volatile compound and could be purified by distillation at 101 °C. It was a colorless liquid of density 1.789 at 16 °C, which became colored under the action of air and light, releasing exceedingly irritating vapors. It was insoluble in water and soluble in alcohol and ether. Aqueous ammonia decomposed it completely at 100° C into propylamine, having a fishy odor. Fuming nitric acid instantly destroyed it with precipitation of iodine. It did not react with cold sulfuric acid but upon heating it decomposed partially into propylene. Allyl iodide in the presence of a little zinc and dilute sulfuric acid decomposed into a gas containing about 25% of propylene. According to Berthelot and de Luca this reaction could be used to prepare propylene. The same reaction in the presence of mercury led to the complete transformation of allyl iodide into propylene (Berthelot & de Luca, 1854).

(2) *Propylene*, C_3H_6 , could be obtained in pure state by collecting the gas disengaged during the reaction of glycerin upon phosphorus iodide, or by the action of mercury and HCl upon propylene iodide. The released gas could be absorbed by fuming or concentrated sulfuric acid. The gas was soluble in glacial acetic acid and in an aqueous solution of cuprous chloride. A mixture of propylene and iodine exposed to the sun for an hour reacted forming a very heavy liquid (density 2.490 at 18.5 °C), which did not solidify when cooled down to -10 °C. Berthelot and de Luca assigned it the formula $\text{C}_6\text{H}_6\text{I}_2$ and named it propylene iodide (Berthelot & de Luca, 1854).

In a following longer memoir, Berthelot and de Luca gave a more detailed explanation of the experimental procedure described above and the analysis, properties, and detection of the different compounds. In addition they presented details about the reaction between hydrogen iodide and glycerin (Berthelot & de Luca, 1855a): Glycerin saturated with HI was maintained during 40 hours in a closed vessel at 100 °C and the resultant product treated with KOH (to neutralize the excess acid) and ether. The dry extract was found to be an iodized liquid, which they named *iodohydrin* (similar to chlorohydrin). Iodohydrin was a golden syrupy liquid, of density 1.783, insoluble in water, sweet, soluble in alcohol and ether, and burning without

leaving residue while disengaging iodine vapors. The results of an elemental analysis corresponded to the formula $C_{12.11}IO$. (Berthelot & de Luca, 1855a).

Berthelot and de Luca's third memoir described the preparation, properties, and composition of allyl and a large number of its derivatives, among them, ethers (e.g. allyl ethyl, allyl phenyl, allyl phenyl, allyl xanthyl, etc.), halogen derivatives (allyl bromide, chloride, and iodide), allyl alcohol, etc. (Berthelot & de Luca, 1856a b). For example, allyl could be prepared by reacting allyl iodide with sodium. The "radical" was a very volatile liquid, having a penetrating odor analogous to that of horseradish, of density 0.684 at 14 °C and boiling at 59 °C (The actual product of the reaction was probably 1,5-hexadiene, boiling at 60 °C). Allyl reacted with halogens in a peculiar form; it combined with chlorine with disengagement of HCl and formation of liquid compound denser than water. Bromine combined instantly with generation of heat and formation of a crystallized bromide, C_3H_5Br . Allyl bromide was a white substance insoluble in water and soluble in ether, and melting at 37 °C. Heated with sodium it decomposed regenerating the allyl. Allyl iodide was prepared by dissolving a large excess of iodine in warm allyl. After a few minutes the whole mixture became solid. This substance was first boiled with aqueous KOH to neutralize the excess iodine and the iodide recrystallized from an ethereal extract. Allyl iodide, C_3H_5I , was sparingly soluble in cold ether and more soluble in boiling ether (Berthelot & de Luca, 1856a b).

Berthelot and de Luca remarked that the formula of allyl iodide (C_3H_5I) differed only by one equivalent of iodine from that of propylene iodide, $C_3H_4I_2$; therefore, they tried unsuccessfully to find a way of converting one compound into the other. For example: (1) the reaction of three parts of iodine (1 equivalent) with 1 part of allyl (1 equivalent) produced the crystallized iodide $C_3H_4I_2$; the mixture retained the odor of allyl but heated with mercury and fuming HCl did not disengage any gas but only the excess of liquid allyl which it contained; (2) hot propylene iodide was able to dissolve a large quantity of iodine; but treatment by an aqueous solution of KOH removed this iodine and caused the propylene iodide to reappear with all its properties; and (3) fuming HCl and mercury converted propylene iodide into propylene but did not react with allyl iodide. Berthelot and de Luca believed that these results proved that propylene iodide, $C_3H_4I_2$, and allyl iodide, C_3H_5I , did not have the same relation between themselves, as the two iodides of mercury; they actually corresponded to two distinct molecular states (Berthelot & de Luca, 1856a b).

ACTION OF THE CHLORIDES AND BROMIDES OF PHOSPHORUS UPON GLYCERIN

Berthelot and de Luca also studied the action of the chlorides and bromides of phosphorus upon glycerin (Berthelot & de Luca, 1856c d). Berthelot (Berthelot, 1853) had already reported that the products of the reaction with phosphorus chlorides were monochlorohydrin C_3H_7ClO , dichlorohydrin $C_3H_6Cl_2O$, and epichlorohydrin C_3H_7ClO and now they were reporting a more detailed study of this particular reaction. The two bromides of phosphorus acted in the same manner upon glycerin; they gave rise to several bromohydrins, all comprised under the general formula $C_3H_7O + HBr - H_2O$. Berthelot and de Luca reported that they had succeeded in isolating monobromohydrin, C_3H_7BrO , epibromohydrin, C_3H_7BrO , dibromohydrin, $C_3H_6Br_2O$, hemibromohydrin $C_{12}H_{27}BrO$, hexaglyceric bromohydrins $C_{26.27}BrO$, acrolein C_3H_4O , a combination of epibromohydrin and phosphine $C_{12}H_{27}BrP$, various liquid substances, volatile *in vacuo* from 200 °C on, which also appeared to be bromohydrins, but which could not be purified; a very small amount of a brominated compound, volatile between 65° and 67 °C, having odor resembling that of allylic ether, etc. (Berthelot & de Luca, 1856c d).

Berthelot and de Luca described in detail the properties of monobromohydrin, epibromohydrin, and dibromohydrin. They also indicated that the reaction of dibromohydrin with ammonia, tin, and phosphorus perbromide yielded glyceramine, C_3H_7NO , and dibromohydrin, C_3H_7BrO . Glyceramine was a liquid very soluble in water and ether and its platinum salt had the formula C_3H_7NO , HCl, PtCl. Dibromohydrin was

a dense liquid distilling at about 180 °C, slowly decomposed by water, and slightly fuming in contact with air (Berthelot & de Luca, 1856c d).

According to Berthelot and de Luca their findings established once more (a) the existence of three distinct series of glyceric compounds, formed by one equivalent of glycerin with 1, 2, and 3 equivalents of acid (b) that besides these three fundamental series there were compounds formed by the combination of one equivalent of acid with several equivalents of glycerin, and (c), the existence of glyceramine, congruent to the analogies of glycerin with alcohol, provided the first example of an alkaloid formed by a sweet substance (Berthelot & de Luca, 1856c d).

Berthelot and de Luca also studied the reaction between glycerin and mixtures of HCl, HBr, and acetic acid, and described a multitude of new derivatives and their preparation method and properties; among them chlorhydridobromohydrin, diacetochlorohydrin, acetodichlorohydrin, acetobromohydrin, acetochlorohydrobromohydrin, etc. (Berthelot & Luca, 1857a, 1858).

CYCLAMEN

De Luca published several papers about the composition of the tubercles of cyclamen (de Luca, 1857a, 1858b, 1872a b). In the first paper he mentioned that the root of this plant was a tubercle of flattened form, brown externally and white internally, and furnished with blackish radicles. The tubercle was known to contain a sweet fermentable substance, starch, gum, and acrid, irritant, and poisonous substances. The extracted juice was acid and extremely astringent and styptic. These facts led de Luca to try to isolate the active principle of this vegetable and determine its main chemical and physiological properties (de Luca, 1857a).

He first washed carefully 4 kg of the tubercles of *Cyclamen europeum* with distilled water, cut them into small pieces and introduced the pieces in a large flask containing 4 liters of rectified alcohol. The mixture was left in the dark for 45 days; afterwards the alcoholic extract was separated by decantation. The process was repeated until the alcoholic extract had no bitter taste. The collected extracts were filtered and then distilled until most of the alcohol had passed over. The resulting jelly residue was left to dry alone and then extracted repeatedly with cold alcohol. The collected extracts were again left to evaporate alone for several days in a cave. The resulting white amorphous solid was exhausted with cold alcohol and then dissolved in boiling alcohol. The resulting extract, on cooling, deposited an amorphous solid, which de Luca assumed was the active principle present in the tubercles, and named *cyclamin*. The cyclamin was dried in the dark by means of concentrated sulfuric acid (de Luca, 1857a).

De Luca described cyclamin as a white, opaque, inodorous, and friable mass, not affected by ordinary reagents. Exposed to humid air it increased in bulk, absorbing a large amount of water. In contact with cold water it assumed the appearance of a milky, viscous, and very adhesive jelly; it dissolved in cold water, and the solution, when agitated, produced an abundant froth like soapy water. De Luca mentioned that the aqueous solution had the remarkable property of coagulating, like albumen, at a temperature of 60° to 75 °C, but this coagulation was only temporary; after two or three days the cold coagulated part redissolved in the mother liquor and could be again coagulated by heat. Analysis indicated that cyclamin did not contain nitrogen, phosphorus, or sulfur; when heated upon a sheet of platinum it left a bulky cinder, which burned completely without residue. Cyclamin was soluble in glycerin, alcohol, the alkalis, and methanol, and insoluble in chloroform, carbon disulfide, essence of turpentine, and the essential oils. An aqueous solution of cyclamin was not colored by iodine and did not ferment with beer yeast; it easily absorbed gaseous bromine and chlorine, coagulating without becoming colored so long as these gases were not in excess. Acetic acid dissolved cyclamin at room temperature and the acid solution did not coagulate upon heating; HCl also dissolved it at room temperature but coagulated it with heat, producing glucose. Nitric acid attacked it at room temperature generating products, which combined with alkalis. The enzyme synaptase split it at 30. to 35. °C producing glucose, which reduced cupric potassium-tartrate and fermented with beer yeast, generating

alcohol and CO₂. According to de Luca, cyclamin contained, by weight, 54.55% carbon, 9.11% hydrogen, and 36.34% oxygen (by difference) (de Luca, 1857a).

It was known that pigs thrived upon the tubercles without any negative effects; de Luca observed that introduction of 10 or even 30 g of the juice in the stomach of a rabbit produced no deleterious effects, but the juice acted as a poison on small fish. He also asked the physician Claude Bernard (1813-1878) to conduct additional tests on the physiological effect of cyclamen juice. Bernard injected fresh juice into the lungs or into the cellular tissue of different animals, such as rabbits, birds, and frogs, in quantities varying from one to four grams, and found that his substance produced death, but less energetically than curare, and with a rather different mechanism. Bernard also reported that the toxic actions of cyclamin and the juice of cyclamen were completely neutralized by the addition of bromine (de Luca, 1857a).

The following paper reported the extraction from the tubercles of cyclamen of a sweet substance having all the properties of mannitol, and some additional properties of cyclamin (de Luca, 1858b). The extracted juice of cyclamen was first filtered, let to ferment, and then boiled to coagulate the cyclamin. The filtrate was evaporated to dryness over a water bath and the solid residue exhausted with cold alcohol. The resulting silky solid appeared as rhomboidal prisms, slightly sweet, stable in humid air, easily soluble in water, melting between 164 ° and 165 °C, decomposing above 250 °C, not fermenting with beer yeast, not reacting with alkalis at 100 °C, and not being reduced by cupric potassium tartrate. A mixture of fuming nitric acid and concentrated sulfuric acid transformed into a nitro compound, and cold nitric acid converted it into oxalic acid. An elemental analysis indicated that its composition corresponded to the formula C₆H₁₂O₆ (with the values of the atomic masses prevalent at that time). De Luca concluded that the set of properties proved that this substance was identical with mannitol. He substantiated this claim indicating that he had conducted parallel comparative examinations with a true sample of mannitol and noticed no significant differences in the results (de Luca, 1858b).

De Luca reported that exposure to light of an aqueous solution of cyclamin led to the gradual precipitation of a white amorphous substance, insoluble in the mother liquid at room temperature, but soluble at a higher temperature. He believed that this new substance was an isomer of cyclamin. He also observed that an aqueous solution of cyclamin, left in contact with air, became covered with purple red vegetation, which the botanist Camille Montagne (1784-1866) identified as a new alga, which he named *Hygrocrocis cyclamina* (de Luca, 1858b). The formation and characteristic properties of this alga were described in detail in a short following note (de Luca, 1872b).

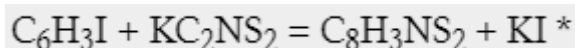
Years later de Luca reported some additional properties of cyclamin, when compared to other proximate vegetable principles. Cyclamin resembled albumin in its property of coagulating by heat; on this coagulate being able, like certain organic calcium salts, of re-dissolving in the mother liquid after it had cooled down and left for a few days, and repeating re-coagulation upon heating. It resembled mannitol in the way it separated from alcoholic solutions; it resembled saponin in the frothing of its aqueous solutions, etc. etc. He also described in more detail the splitting of cyclamin into cyclamiretin and glucose, and glucose and mannitol (de Luca, 1872a b, 1878). An aqueous solution of cyclamin was not fermented by beer yeast and was not reduced by copper salts; nevertheless, abandoned to itself for a long time it split into glucose and mannitol, two substances easily separable. After a longer time the glucose fermented and the remaining liquid was found to contain mannitol, having all the properties of commercially available mannitol. All these results indicated that cyclamin was a glucoside, from which it was possible to obtain not only glucose (as all other glucosides), but also an additional sugar (mannitol) (de Luca, 1878).

ARTIFICIAL MUSTARD OIL

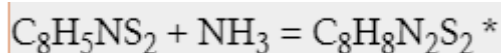
In 1855 Berthelot and de Luca reported that they had succeeded in synthesizing mustard oil using the results they had obtained during the synthesis of allyl iodide (Berthelot & de Luca, 1855c). They wrote that

the essence of mustard had been investigated by many chemists, particularly because of the large number of its derivatives, which could be prepared; its physiological effects, and its similarity with the essence of garlic, produced naturally from many brassicacea. In particular, they mentioned that Dumas and Pelouze had analyzed garlic oil, determined the density of its vapor, and many of its properties. This oil absorbed rapidly ammonia and formed thiosinamine (1-allyl-2-thiourea), a white crystalline compound, melting at 70 .C and very soluble in water, alcohol, and ether (Dumas & Pelouze, 1833). Years later, Theodor Wertheim (1820-1864) proved that the essence of mustard (C.H.N.S.; today C.H.NS, allyl isothiocyanate) could be considered a compound of garlic oil and hydrosulfocyanic acid (Wertheim, 1844).

In a previous memory, Berthelot and de Luca had shown that glycerin treated with phosphorus iodide furnished allyl iodide, having a formula (C.H.I, today C.H.I) very similar to that of garlic essence (C.H.S), where a sulfur atom had substituted the iodine atom. Hence, all it was necessary was to effect this substitution and then to combine the product with hydrosulfocyanic acid to produce oil of mustard. Berthelot carried this double reaction in one step by treating allyl iodide with potassium sulfocyanate (thiocyanate) in a closed vessel at 100 .C:



According to Berthelot and de Luca, the resulting liquid had all the known properties of essence of mustard; it exerted the same irritating action upon the eyes and skin, boiled at the same temperature, and when treated with ammonia furnished thiosinamine in the same manner:



In an additional paper, Berthelot and de Luca reported a detailed study of the crystals of synthetic and artificial thiosinamine, showing that both compounds were identical (Berthelot & de Luca, 1855d).

PLANT PRINCIPLES

Tangerine

According to de Luca, the essence contained in the peels of tangerine was not commercially available, probably because of the high price of the fruit. This was also the reason why it had not been chemically examined (de Luca, 1857b).

De Luca obtained from a friend 500 pieces of fruit from which he separated the juice by expression. The resulting liquid had a slight gold yellow color, was limpid and highly mobile, its odor was quite different from that of the orange and pear lemon, not disagreeable, it distilled at about 178 .C, and left a small quantity of residue containing the coloring matter. The distillate was colorless and had the same odor and taste like the original juice; it was lighter than water and had a density of 0.852 at 10 .C. It was insoluble in water and soluble in alcohol, carbon disulfide, ether, and glacial acetic acid. It dissolved iodine, bromine, resins, oils, beeswax, phosphorus, and sulfur. The essence did not seem to contain oxygen. Elemental analysis indicated it contained, by weight, 87.54% carbon and 12.46% hydrogen, corresponding to the formula $\text{C}_{20.16}$. Addition of cold concentrated sulfuric acid turned it red and the color disappeared on addition of water. Hot sulfuric acid charred it with release of SO_2 . Nitric acid did not turn it red while hot acid attacked it promptly, with release of nitrous vapors. Cold and dry HCl gas produced a brown coloration; addition of a concentrated solution of the acid precipitated a crystalline matter having the formula $\text{C}_{20.16}, 2\text{H}_2\text{O}$. The essence was dextrorotatory, with rotatory power $\alpha = 85.5$ (de Luca, 1857b). The pure essence and its alcoholic, acetic,

ethereal, etc. solutions were fluorescent, but not the crude juice. De Luca believed that the yellow coloring matter of the latter masked the effect (de Luca, 1857b).

Pear lemon (*Citrus lumia*)

De Luca obtained the essence of this fruit by expression and reported that it was a deep yellow juice, which on distillation left the coloring matter in the retort. The first fractions, passing between 130. and 180 .C, contained water; the fractions distilling about 220 .C were accompanied by white vapors having an empyreumatic odor. The distilled essence was always limpid and colorless; the fraction passing between 180. and 190 .C had a density of 0.912 at 10 .C; a second distillation of this fraction produced a liquid boiling at 180 .C and density 0.853 at 18 .C; it was insoluble in water and soluble in alcohol, carbon disulfide, and ether. Elemental analysis indicated that it contained, by weight, 87.82% carbon and 12.18% hydrogen, corresponding to the formula $C_{20.16}$; treatment of its alcoholic solution with nitric acid deposited after some time a crystalline deposit of the hydrate. The essence was dextrorotatory with a rotatory power $\alpha = 34$ (de Luca, 1860d).

Sweet maudlin (*Achillea ageratum*)

De Luca separated the essence sweet maudlin by steam distillation of the flowers and contacted a small amount of it with large a quantity of oxygen in a graduated tube. No decrease in the volume of the gas was noted; even when the essence was heated alone or in the presence of platinum black (de Luca, 1875). Contact with a solution of sodium sulfite caused the essence to become milky during many days. When distilled, the fraction passing between 165. and 170 .C remained liquid even when cooled to -18 .C. The essence had a density of 0.849 at 24 .C; elemental analysis indicated that it contained, by weight, 76.45 to 77.65% of carbon, 11.31 to 11.51% of hydrogen, and 11.04 to 12.14% of oxygen, corresponding to the formula $C_{26.44}O_{..}$. The small amount of essence available did not allow de Luca to determine its chemical functions (de Luca, 1875).

Phillyrrea latifolia (green olive tree)

Cesare Bertagnini (1827-1857) and de Luca wrote that the bark of *Phillyrrea latifolia* contained a crystallizable principle, *phillyrin*, which had been discovered by the pharmacist Carboncelli. Bertagnini and de Luca extracted it by cooking the bark with a diluted solution of calcium sulfate or with powdered lead oxide. The resulting solution was filtered and the liquid concentrated by evaporation. Left to evaporate by itself it deposited crystalline phillyrin, which was purified by further crystallization from water and alcohol. The pure extract was snow white, bitter, odorless, slightly soluble in cold water and very soluble in boiling water, soluble in alcohol, and insoluble in ether. The mother liquor contained mannitol, identical to that extracted from manna; it crystallized as rhomboidal prisms, soluble in water and alcohol, melting between 164. and 165 .C, and having a composition equivalent to the formula $C.H.O.$ (Bertagnini & de Luca, 1860b).

Bertagnini and de Luca reported that phillyrin contained water, which it lost at temperatures below 100 .C or by exposure to concentrated sulfuric acid in a limited atmosphere. The elemental composition of the dry principle indicated it contained, by weight, 60.53% carbon, 6.37% hydrogen, and 33.06% oxygen, corresponding to the formula $C_{54.34.22}$ (today, 60.66% carbon, 6.41% hydrogen, and 32.92% oxygen; $C_{27.34.11}$). Phillyrin melted at 160 .C and at higher temperature it decomposed releasing flammable gases and empyreumatic vapors, and leaving a carbonaceous residue. Phillyrin was completely soluble in cold

concentrated sulfuric acid, producing a red violet solution, which in contact with humid air became colorless and started depositing a substance that contained glucose. Phillyrine reacted with chlorine and bromine producing the pertinent halogen derivatives easily crystallizable. Bertagnini and de Luca believed that the principle should be considered a glucoside, because it was not reduced by cupro-potassium tartrate and did not ferment with beer yeast. It did do after being decomposed into glucose and *phillygenine*, $C_{42.24.12}$, by hot diluted acids (Bertagnini & de Luca, 1860b).

Stigmaphyllon jatrophæfolium

De Luca and Giuseppe Ubaldini found that the tubercles of this plant contained a principle identical from the one extracted from asparagus (asparagin) (de Luca & Ubaldini, 1864).

HEPATIC SUGAR

Little information was available about this sugar although Bernard had shown that the glycogenic matter of the liver could be converted into a particular glucose, (Bernard, 1853). It was not known if it was identical with one or more of the common glucoses, such as those of grape, malt, levoglucose, and milk. These facts led Berthelot and de Luca to do some experiments on the subject. They obtained a sample of the crystalline combination of hepatic glucose with sodium chloride and reported that this glucose appeared as voluminous crystals, limpid and colorless, unable to reduce cupro-potassium tartrate and ferment under the influence of malt yeast (Berthelot & de Luca, 1859). They had a dextrorotatory power $\alpha = 47^\circ$, which increased substantially during the first moments after they were dissolved in water. They contained 3% by weight of chlorine, figure that agreed well with the formula $2C_{12.12.12}, 2HO + NaCl$. According to Berthelot and de Luca these properties agreed exactly with those of the combination of grape sugar and sodium chloride (Berthelot & de Luca, 1859).

The following year de Luca had the opportunity of examining the liver of a person who had died from cerebral congestion and had a partially atrophied pancreas (de Luca, 1860c). He washed the liver with distilled water and found that the liquid dissolved a substance capable of reducing cupro-potassium tartrate and fermenting in contact with yeast beer. He also observed that the washed liver after standing for many hours produced a new quantity of sugar, indicating that the liver contained a substance able to transform into sugar with time, and under the sole contact of substances present in the organ. De Luca eliminated from the liver all the substances soluble in water, then ground it in a mortar, heated it moderately, and left it in contact with a small amount of water. This process released a milky substance containing in suspension a white substance able to cross a filter the same as a starch solution. The liquid was unable to reduce the cupro-potassium tartrate reagent but tinted iodine and became limpid and transparent after being in contact with saliva. In this state, it was able to reduce the tartrate reagent and ferment with malt yeast. The same milky suspension treated first with a few drops of HCl and then with a diluted solution of sodium chloride, reduced the tartrate reagent and fermented with the yeast. Left to evaporate alone, it precipitated crystals, which contained less chlorine than the amount present in sodium chloride. These crystals represented the combination of the glucose present in the glycogenic matter of the liver with sodium chloride.

According to de Luca, all these results proved that the disease of the pancreas did not affect the glycogenic function of the liver (de Luca, 1860c).

REACTION BETWEEN SO. AND H₂S

According to de Luca and Joseph Ubaldini, sulfur dioxide and hydrogen sulfide did not react if dry and at room temperature, but in the presence of water they produced water and deposited sulfur, a reaction that explained the origin of certain sulfur deposits like the one in Pozzuoli, near Naples, and every place where there was a simultaneous disengagement of H₂S, SO₂, and water (de Luca & Ubaldini, 1867). General opinion was that two volumes of the acid reacted with one of dioxide to generate 2 equivalents of water and 3 of sulfur, but de Luca and Ubaldini believed that the actual reaction was much more complex because it involved the initial formation of pentathionic acid, followed by its decomposition into sulfur and other substances. Chemical examination of the sulfur generated was not reliable enough because part of it was present as very small particles, which deposited very slowly, and only part of the solid was soluble in carbon disulfide. De Luca and Ubaldini believed that to find the correct ratio of the products of the reaction (water and sulfur) required employing a large amount of the solution of H₂S and a small amount of SO₂. For this reason they mixed in a stoppered bottle a solution containing a weight of 1.700 g of hydrogen sulfur in 613.5 cm.³ of water, with another containing 1.6 g of SO₂ in 54 cm.³ of water (corresponding to 2 volumes of acid per volume of dioxide). The resulting milky liquid was clarified with carbon disulfide and the sulfide phase was separated, filtered, and evaporated in a water-bath. The resulting sulfur deposit was dried and weighed. De Luca and Ubaldini found that in some cases about two equivalents of soluble sulfur were obtained, while in others insoluble sulfur separated in greatest proportion. These discrepancies were attributed to experimental factors hard to control, such as the amount of agitation, the temperature of the liquid, the light, contact, time, excess of one or the other constituent, etc. (de Luca & Ubaldini, 1867).

It was known that in this reaction acids of the thionic series were formed and Berthelot had shown that the sulfur separated from pentathionic acid should be the insoluble variety (Berthelot, 1864). Since SO₂ was known to increase the stability of insoluble sulfur it was to be expected that the presence of an excess of the dioxide would result in a proportion of insoluble sulfur greater than when the substances used were used in equivalent proportions.

De Luca and Ubaldini reported that a solution of sodium chloride, shaken with the mixture of the two solutions, precipitated the suspended sulfur and clarified the liquid. Oxidation of the filtrated liquid with potassium chlorate and HCl transformed the sulfur of the thionic acid into sulfuric acid, easily quantified as barium sulfate. Combination of both steps allowed determining the total amount of sulfur (de Luca & Ubaldini, 1867).

De Luca and Ubaldini concluded that the results of their experiments proved that the sulfur deposited by the reciprocal action of SO₂ and hydrogen sulfide consisted of two varieties, one soluble and the other insoluble in carbon disulfide, and the proportion between these two varieties depended not only on the substances taken, but also on the operating conditions (de Luca & Ubaldini, 1867).

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