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REVIEW ARTICLE

VICTOR-JOSEPH-HIPPOLYTE DE LUYNES: Erythritol, butylene, and dyes
VICTOR-JOSEPH-HIPPOLYTE DE LUYNES: Eritritol, Butileno, y Tintes

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ABSTRACT

Victor-Joseph-Hippolyte Luynes (1828-1904) was a French chemist who studied in great detail erythritol and its derivatives, examined its oxidation with chlorine, phosphorus iodide, and acids, as well as the properties of some of the corresponding products (i.e. dichloroerythrite and iodoerythrite). Luynes proved that this compound was a tetrol belonging to the butylic series and having properties very similar to the other alcoholic series. This finding led him to study the preparation and properties of butylene, which Faraday had first obtained by decomposing fatty materials by heat. Luynes showed that it could also be prepared by decomposing butyl iodide by means of silver acetate or an alcoholic solution of KOH. With Esperandieu he investigated the preparation and properties of pyrogallic acid (used in photography, hair treatment, tanning, etc.), and a series of its derivatives, the properties and reactions of orcin (orcinol), particularly its reaction with ammonia, which transformed it into orcein, a coloring matter that did not turn red in the presence of acids, and litmus. Together with Persoz and Salvétat they discovered Paris blue, a dye resistant to acids and to light.

Keywords: Butylene; erythritol; litmus; orcin; pyrogallic acid.

RESUMEN

Victor-Joseph-Hippolyte Luynes (1828-1904) fue un químico francés que estudió en detalle el eritritol y sus derivados, examinó su oxidación con cloro, ioduro de fósforo y ácidos, así como las propiedades de algunos de los productos correspondientes (i.e. dicloroeritritol and iodoeritritol). Luynes probó que este compuesto era un tetra alcohol perteneciente a la serie butílica que poseía propiedades muy similares a las de otras series alcohólicas. Este descubrimiento lo llevó a estudiar la preparación y propiedades del butileno, que Faraday había preparado por primera vez calentando materias grasas. Luynes demostró que también podía ser preparado mediante la descomposición del ioduro de butilo por el acetato de plata o una solución alcohólica de KOH. Luynes y Esperandieu estudiaron la preparación y propiedades del ácido pirogálico (usado en fotografía, tratamiento del cabello, curtido, etc.) y una serie de sus derivados; las propiedades y reacciones de orcina (orcinol), en especial, su reacción con amoníaco que la transformaba en orceina, un colorante que no enrojece en presencia de ácidos, y el litmus. Junto con Persoz y Salvétat descubrieron el azul de Paris, una tintura resistente a los ácidos y la luz.

Palabras clave: ácido pirogálico; butileno; eritritol; litmus; orcina.

INTRODUCCION

Life and work (Winter, 1909; Emptoz, 1994; Anonymous, 2016)

Victor-Joseph-Hippolyte Luynes was born in Paris on 16 of April 1828, son of Laurent de Luynes, the general secretary of the Ministry of Public Instruction, and Sophie Charlotte Fessard. After finishing his basic education at collège Stanislas (bachelier ès lettres et ès sciences mathématiques), he enrolled in the Faculty of Sciences of Paris from where he obtained his licencié ès sciences physiques and his degree of docteur ès sciences physiques (1864), after successfully defending a thesis about erythrite and its derivatives (Luynes, 1864a). This work earned him the Jecker Prize of the Académie des Sciences. In between these degrees, he served as professeur répétiteur of physics and chemistry (1849) and professor of physics and chemistry at the lycée Bonaparte (1852-1855), préparateur de Michel Eugène Chevreul (1786-1889) at the Muséum d'Histoire Naturelle (1850), and préparateur of Jean-Baptiste André Dumas (1800-1884) at the Sorbonne (1855). In 1862 he was appointed préparateur at the Laboratoire de Recherches et Perfectionnement of the Faculty of Sciences of Paris [replacing the chemist Henri Étienne Paul Bérard (1836-1921)], and in 1868 he was promoted to head of the laboratory. In 1868 he was appointed adjunct professor of Louis Pasteur (1822-1895) at the Faculty of Sciences; at the death of Jean-François Persoz (1805-1868) in 1868, he replaced him at the Chair of Dyeing, Apprêt et Impression des Tissus at the Conservatoire des Arts et Métiers.

In November 14, 1859, Luynes married Antonie Huard, the daughter of a Parisian lawyer. Luynes died on August 6, 1904 at Meudon (Seine et Oise) and was buried at the Montparnasse cemetery.

Luynes was very active in public activities. In 1863 he was elected member of the Société Philomatique of Paris. In 1874 he was appointed head of the sugar analysis laboratory of the Direction Générale des Douanes (which afterwards became the laboratory of the Ministry of Finances), a position he kept until November 1903. In 1878 he replaced Claude Auguste Lamy (1820-1878) at the Conseil d'Hygiène et Salubrité. Luynes was vice president of the Société d'Encouragement pour l'Industrie Nationale, member of the organizing committee and judge of prizes of the Universal Expositions of Paris and abroad. The French government appointed him to report about the advances on ceramics presented at the international Expositions of London (1872) and Vienna (1874). In 1874 he was appointed chevalier of the Légion d'Honneur and in 1888 he was promoted to officier.

Scientific contribution

Luynes wrote about 40 papers and books (e.g. Luynes, 1882; Persoz et. at, 1861c; Berthelot et al., 1866) on the subjects of inorganic, industrial, and organic chemistry, lichens, natural products, and dyes. He also wrote a booklet describing his research and main scientific achievements, as customary for candidates to scientific institutions (Luynes, 1868a). In addition to the subjects described below he also studied the extraction of bismuth from alloys (Luynes, 1862b); the use of hydrogen iodide in organic chemistry (Luynes & Salet 1864); the diffusion of bodies (Luynes, 1869); glass, glass tempering, and glass drops (Luynes, 1872b, 1873, 1877; Luynes & Feil, 1875); boric acid (Luynes, 1872a, 1875); the rotatory power of crystalline sugar (Luynes & Girard, 1875); etc.

In all that follows it is necessary to take into account that Luynes used as atomic masses C = 6; O = 8; H = 1; Cl = 35.5; and P = 31, in all his chemical reactions and formulas.

Arsenic and derivatives

In a first note on the subject Luynes wrote that Jöns Jacob Berzelius (1779-1848) had recommended that pure arsenious acid (arsenic trioxide) could be easily prepared by agitating the commercial product with ammonia, for several hours at 700 to 80 0C, in a closed vessel. The resulting liquid was left to stand for a few moments and then transferred to another bottle. On cooling, octahedral crystals of arsenic trioxide, free of ammonia, were deposited

Luynes, 1857a.

Luynes repeated Berzelius' process without success. He obtained an abundant deposit of crystals, but these did not show the properties of arsenious acid. He noticed that leaving the crystals in contact with the mother liquor in an open vessel they gradually dissolved until they disappeared completely; the ammonia was released slowly in the air until the remaining liquor did to not smell like it, although it showed a strong alkaline reaction. Finally, a second deposit was formed of crystals less transparent than the former octahedral ones. Chemical analysis showed that the new crystals were pure arsenious acid containing no ammonia. Luynes repeated the experiment, this time separating the first crystals formed; inspection showed that all were shaped as well-defined prismatic needles, containing no octahedral ones and having a strong ammoniacal odor. Luynes drained the crystals and dried them between sheets of paper. Chemical analysis indicated they contained, by weight, 8.67% water, 13.40%, ammonia, and 77.93% arsenious acid; a composition quite similar to that of ammonium arsenite (Luynes, 1857a). Luynes justified his conclusion quoting the results obtained by Louis Pasteur in his study of arsenious chloride and some arsenites (Pasteur, 1848). Pasteur reported that addition of concentrated ammonia to arsenious trioxide resulted in the immediate formation of crystalline ammonium arsenite, shaped as an oblique prism of rectangular base and highly unstable in contact with air: all the ammonia disappeared after a day or so leaving a mass of powdered arsenious trioxide.

Luynes also studied in detail the properties of arsenic trioxide (Luynes, 1857b). He heated a mixture of arsenious acid and ammonium chloride and noticed that initially a large amount of ammonia was released, followed by white fumes. This result was very different from the reaction between a chloride and an acid, but could be easily understood considering that the reaction between arsenious acid and HCl gave water and arsenic trichloride:

AsO2 + 3HCl = AsCl3 + 3HO

Pasteur used this reaction to prepare arsenic trichloride.

According to Luynes, a similar phenomenon happened during the reaction between arsenious acid and ammonium chloride. Observation of the contents of the flask showed that after release of the gas had ceased, the upper part of the flask was covered mostly with arsenious acid, a result of this compound being more volatile than ammonium chloride. This difference in volatility prevented the contact between the two reagents and limited the duration of the period of gas disengagement. Luynes believed that a second explanation was also possible: When the flask was opened, after cooling, white and highly acid fumes, similar to those given by arsenic trichloride, were released. Treatment of the solid residue with water interrupted this release while generating a highly acid liquid. The acidity was caused by HCl, which resulted from the decomposition by the water of the arsenic trichloride produced during the experiment. Hence, during the first part of the reaction the ammonia was eliminated on account of the affinity of arsenious acid for HCl, and chloride (or perhaps oxychloride) of arsenic was formed. The large amount of the latter resulted in the inverse reaction, which opposed the continuation of the process. Arsenious acid acted then on ammonium chloride like the metallic oxides: ammonia was liberated accompanied by the formation of chloride and water (Luynes, 1857b).

In another paper Luynes reported that he had synthesized a new combination between arsenic trichloride and ethanol (Luynes, 1860). He found that mixing arsenic trichloride with absolute alcohol resulted in a very exothermic reaction that elevated the temperature to about 70 0C. Distillation of the product resulted in the passing of a fraction, boiling at 148 0C, which turned out to be a combination of the chloride with the alcohol. Bubbling HCl through a suspension of arsenic trichloride in alcohol resulted in the same product. In this case the temperature increased as the chloride dissolved, and eventually the liquid separated into two layers. The lower layer begun boiling at 96 0C and then the temperature increased until it stabilized at 148 0C. The latter fraction was colorless, fuming in air and decomposed by water into HCl, arsenic trichloride, and alcohol. It also decomposed rapidly in contact with air. Chemical analysis of the compound indicated that it contained, by weight, 9.5 to 9.6% carbon, 2.1 to 2.7% hydrogen, 47.6 to 47.7% chlorine, and 34.5% arsenic, corresponding to the formula C4H6O2,AsCl3. Luynes remarked that methanol and amyl alcohol seemed to produce the same compound (Luynes, 1860).

Erythrite (Erythritol, 1,2,3,4-butanetetrol)

Luynes wrote several papers about this polyol and its derivatives (Luynes, 1862a, 1863b, 1864def) and, eventually, his doctoral thesis (Luynes, 1864a). In one of his publications he reviewed the historical discovery of the different members of the alcohol series, including polyalcohols (Luynes, 1864a). Between 1834 and 1836 Dumas and Eugène Melchior Péligot (1811-1890) proved that wood spirit was a compound which differed from common alcohol, (spirit de vin) in having less carbon and hydrogen but having physical and chemical properties very similar to those of ordinary alcohol, Dumas and Péligot studied many of its reactions, including formation of esters and dehydration with concentrated sulfuric acid, and concluded that wood spirit was an alcohol, which they named methylic alcohol (Dumas and Péligot, 1834, 1836). Further researchers discovered additional members to the alcohol series. Marcelin Berthelot (1827-1907) found that glycerin behaved like an alcohol capable of forming combinations triple than those of ordinary alcohol, showing that glycerin was a triol (Berthelot, 1854). Shortly thereafter, Charles Würtz (1817-1884) discovered the glycols31 (Würtz, 1856) and Berthelot, mannitol, a hexol (Berthelot, 1856). Luynes summarized the information available about polyols, saying that, so far, were known (a) four diols (glycol, propylglycol, butylglycol, and amylglycol), (b) one triol (glycerin), and (c) one hexol (mannitol). In addition, Berthelot had shown that within the sugars, there were several substances that seemed to function as polyols. One of then was erythrite (known also as pseudoorcine, erythoglucine, erythromannite or phycite), for which its functionality had not been determined definitely. Luynes wrote that his results indicated that this compound was a tetrol belonging to the butylic series having properties very similar to the other alcoholic series (Luynes, 1862a, 1864a).

In 1848 John Stenhouse (1809-1880) discovered erythrite (present as erythric acid, a combination of erythrite and orcin) in the lichen Rocella montagnei (Stenhouse, 1848) and in 1857 Lamy found it, in a free state, in the lichen Protococcus vulgaris (Lamy, 1857). Stenhouse extracted the active principle from the lichen by maceration with a large amount of water for some hours, followed by addition of quicklime, repose, and filtration. The resulting extract was then boiled for two or more hours in an open pan until concentrated to a third or fourth of its original volume; and the remaining calcium precipitated by means of a stream of CO2. The filtrate was then evaporated over a water bath to thick syrup, consisting mainly of orcin, erythrite, and a reddish coloring matter. The syrup was mixed with about three times its volume of alcohol and then left alone. After standing for about two days, the

erythrite crystallized as small brilliant crystals and was purified by repeated crystallization from boiling alcohol (Stenhouse, 1848).

Lamy extracted Protococcus vulgaris with boiling water for several hours, evaporated the filtrate to viscous syrup, added concentrated alcohol to precipitate the gummy material, and slowly concentrated the new filtrate to precipitate crystals of erythrite (Lamy, 1857).

Erythrite crystallized as straight prisms of square base, very hard and slightly sweet, and melting at 120 0C. It was very soluble in water and in boiling absolute alcohol; the aqueous solution did not deviate polarized light. It combined with tartaric acid at 100 0C, and with stearic, benzoic, and malic acids at temperatures between 2000 and 250 0C. These and other properties proved that erythrite behaved like a substance intermediate between mannitol and glycerin. According to Berthelot erythrite should be considered a tetrol or a hexol, with possible formulas C8H10O8 or C12H15O12, respectively, while Stenhouse believed that the correct formula was the first one, C8H10O8 (Stenhouse, 1862).

According to Luynes, Stenhouse's procedure was appropriate only for preparing small amounts of erythrite. Preparation of larger amounts required treating a substantial mass of lichens, handling large volumes of calcium extract, and the prolonged time of evaporation resulted in the oxidation of orcin and increase in the amount of resinous matter. For these reasons Luynes modified the procedure as follows: The lichens were macerated for one hour in large containers with ordinary water to impregnate them completely; a small amount of diluted lime solution was then added and the whole heated strongly. The liquid was separated and treated with a slight excess of HCl, which precipitated the erythric acid as a thick jelly. This jelly was mixed with calcium carbonate and the mixture heated for several hours in a closed vessel at 150 0C, in order to decompose the erythric acid into orcin and erythrite, which remained in the liquor. The erythrite was purified as described before and found to have the same properties as the material obtained by other methods. Luynes added that calcium carbonate was more soluble in an aqueous solution of erythrite than in pure water. The resulting solution was coagulated by heat or by addition of absolute alcohol. Luynes found that the amount of calcium carbonate dissolved was not proportional to the concentration of erythrite (Luynes, 1864a).

Luynes studied the reaction of erythrite with several oxidation agents, chlorine, phosphorus iodide, and acids, and determined the properties of some of the corresponding products. Oxygen did not affect erythrite under normal conditions, but under the influence of platinum black, a concentrated aqueous solution of erythrite absorbed oxygen so energetically that the mass became incandescent. The reaction of a diluted solution was not so strong and resulted in the formation of an acid similar to the one obtained with mannitol. At 240 0C, erythrite reacted with KOH forming oxalic and acetic acids and releasing a large amount of hydrogen gas. Chlorine, under the influence of daylight, reacted with erythrite forming HCl and dichloroerythrite, a viscous non-crystallizable substance. Phosphorus pentachloride produced the same results, while phosphorus triiodide carbonized most of erythrite. Hydrogen chloride produced a crystalline product (Luynes, 1864a).

Luynes wrote that dichloroerythrite was a white crystalline mass, bitter, soluble in water, alcohol, and ether, melting at 145 0C and releasing white fumes at higher temperatures. Elemental analysis indicated that it contained, by weight, 30.2% carbon, 5.5% hydrogen, 19.9 oxygen, and 44.4% chlorine, corresponding to the formula C8H8Cl2O4 (Luynes, 1864a).

Iodoerythrite was prepared by heating in a tubulated retort 30 g of very dry erythrite and 350 to 400 g of fuming hydrogen iodide (Luynes, 1864ae). The first passing fraction was a small amount of HI, which was received over water, accompanied by an oily substance that

deposited at the bottom of the receiver and was found to be impure butylene iodide. This compound was separated and washed first with a concentrated solution of KOH and then with abundant water. The results indicated that 10 g of erythrite yielded about 17 g of impure butylene iodide. The wet iodide was dried over calcium chloride followed by distillation. Luynes remarked that better results were obtained adding a small amount of red phosphorus to the reaction mixture. The liberated iodine, in contact with the phosphorus, regenerated HI so that the mixture was always saturated with gas, allowing a complete reduction of the erythrite. According to Luynes, butylene iodide was liquid at room temperature, colorless and having an agreeable ethereal odor. It had relative density of 1.632 at 0 0C and boiled at 118 0C at room pressure. It was insoluble in water and soluble in alcohol and ether. Chlorine decomposed it liberating iodine and a compound, which seemed to be butylene dichloride, C8H8Cl2. The reaction between butylene iodide and bromine was very strong, liberating iodine and HBr, and a colorless liquid, insoluble in water, soluble in alcohol and ether, and boiling at 158 0C at room pressure. Chemical analysis indicated that it contained, by weight, 22.15% carbon, 4.05% hydrogen, and 73.8% bromine, corresponding to the formula C8H8Br2, that is, butylene dibromide (Luynes, 1864ae).

The results of these and some additional reactions indicated that erythrite should be considered a tetrol (Luynes, 1862a, 1864a).

Luynes also studied the preparation and properties of butylene, C8H8 (Luynes, 1863c, 1864af), a compound that Michael Faraday (1791-1867) had been the first to obtain, by decomposing fatty materials by heat (Faraday, 1825). Luynes prepared it by decomposing butyl iodide, C8H9I, by means of silver acetate or an alcoholic solution of KOH. Use of silver acetate had the advantage of producing also butyl acetate. The procedure involved heating in a sealed tube a mixture of 20 g of silver acetate and 20 g of butyl iodide and letting the reaction proceed by itself for about one to two hours (the paper includes a drawing of the apparatus). Luynes wrote that at room temperature butylene was a gas smelling like garlic, sparingly soluble in water and more in ether, very soluble in acetic acid, boiling at 3 0C (this value is close to the boiling point of cis-2-butene, 3 0C), and solidifying at the low temperature provided by a mixture of solid CO2 and ether. Butylene acetate was a colorless liquid, lighter than water, having a pleasant aromatic and penetrating odor, different from the fruit smell of butyl acetate, boiling between 1110 and 113 0C, and found to contain, by weight, 61.5% carbon, 10.9% hydrogen, and 27.6% oxygen. Butylene reacted readily with bromine yielding butylene dibromide, C8H8Br2. Butylene iodide and silver oxide reacted slowly at room temperature, and very rapidly at 100 0C, producing silver iodide, butylene, and a complex liquid, lighter than water. Distillation of the latter passed, at 950 to 100 0C, a liquid fraction containing, by weight, 64.33% carbon, 13.9% hydrogen, and 21.77% oxygen, corresponding to butylene hydrate (butan-2-ol). This compound was colorless, had a strong and penetrating smell and relative density 0.85 at 0 0C, and was very soluble in water. Bromine attacked it yielding a complex mixture of products that boiled between 1300 and 158 0C. The hydrate reacted with iodine forming an iodide identical with butylene iodide. Heated in closed tube to 250 0C it decomposed into water and butylene (Luynes, 1863c, 1864b).

Pyrogallic acid

In 1865 and 1867 Luynes and G. Esperandieu published the results of their research about the preparation and properties of pyrogallic acid (Luynes & Esperandieu, 1865, 1867). Several famous scientists had extensively studied this acid [e.g. Berzelius, Henri Braconnot (1780-1855), Chevreul, Justus von Liebig (1803-1883), Théophile-Jules Pelouze (1807-1867), etc.], and had discovered important uses for it (photography, hair treatment, tanning, etc.).

According to Pelouze, gallic acid, heated to 210 0C in a retort, decomposed completely into pyrogallic acid and CO2 according to the reaction

C14H6O10 = C12H6O6 + CO2

This reaction could also be conducted by dropping crystals of gallic acid on mercury heated to 210 0C (Pelouze, 1833). In practice, the process was highly inefficient, 100 parts of gallic acid yielded 25 of pyrogallic acid, instead of the theoretical 74.1 parts. The yield had been improved somewhat by separating the pyrogallic acid by sublimation (Stenhouse, 1843), or by heating gallic acid over pumice stone and subliming the pyrogallic acid by means of a

CO2 stream (Liebig, 1857).

According to Luynes and Esperandieu, the low yield was a result of the thermal instability of pyrogallic acid at the temperature used in Pelouze's procedure. Pyrogallic acid could be distilled without decomposition temperatures below 200 0C, but was almost completely destroyed when heated at higher temperatures for a long time (as in distillation). Accordingly, they explored the possibility of decomposing gallic acid in closed vessels by means of water and bases. The results were satisfactory but the procedure to eliminate the base resulted too complicated. For this reason they decided to test the possibility of using only water as the vehicle for decomposition. In their experiments they put a mixture of one part of gallic acid with two or three of water, in a brass cauldron with a tightly fitting cover, and heated everything at 2000 to 210 0C for 1.5 to 2 hours. To their satisfaction, the process resulted in the complete decomposition of gallic acid into pyrogallic acid and CO2. The product was a slightly colored solution of pyrogallic acid, which was decolorized by boiling with animal black. The bleached solution was filtered and concentrated by evaporation. Upon cooling the pyrogallic acid solidified in the form of a hard crystalline mass, slightly amber, and sometimes colored rose. Distillation under vacuum (20-30 mmHg) was enough to produce a white product. The yield of pyrogallic acid obtained by this process was practically identical with the theoretical one. The product of this new process was found to have the same properties as the one obtained by sublimation (Luynes & Esperandieu, 1865, 1867).

Luynes and Esperandieu prepared a series of derivatives of pyrogallic acid. For example, ammonium pyrogallate was obtained by reacting a solution of pyrogallic acid with an excess of ammonium carbonate. The resulting solution was then evaporated to dryness, the residue dissolved in ether, and the crystalline salt reprecipitated by means of a stream of ammonia gas. According to Luynes and Esperandieu, ammonium pyrogallate was a white salt, containing, by weight, 11.87% ammonia, corresponding to the formula C12H6O6NH3. It was known that a solution of pyrogallic acid added to limewater, gave rise to a superb violent coloration, which disappeared shortly after formation. Luynes and Esperandieu found that the same coloration appeared when breaking the still humid pieces of calcium pyrogallate produced by the decomposition of pyrogallic acid by lime in a closed vessel. Ethylamine caused the same coloration. Acetyl chloride reacted with pyrogallic acid releasing HCl and forming a crystalline product composed of acetic acid and pyrogallic acid. A concentrated slightly acid solution of quinine, added to a concentrated aqueous solution of pyrogallic acid, produced a yellowish crystalline deposit, which contained the elements of quinine sulfate and pyrogallic acid and was highly resistant to crystallization. Orcin and resorcinol reacted just in the same way with quinine sulfate of quinine, whence this reaction with sulfate of quinine would appear to be common to those substances designated as phenols (Luynes & Esperandieu, 1865, 1867).

Orcin (orcinol) and orcein

Luynes did extensive research on orcin, its properties and reactions (Luynes, 1863ad, 1865ab, 1868bc; Luynes & Lionet, 1867a). Orcein is a coloring substance that is present already formed in several lichens, but is usually obtained by reacting evernic, erythric, or orsellic acid with boiling alkali. In his first paper (Luynes, 1863ad) Luynes mentioned that Pierre Jean Robiquet (1780-1840) had isolated orcin in 1829 using a process based on successive macerations of the lichen with concentrated alcohol and purification of the extract. The purified extract was found to be composed of two different substances, one formed of needle-shaped white crystals, the other by a green acrid tasting resin. The crystals were found to contain ammonium and calcium oxalates and two white substances, variolarin and orcin [3,5-dihydroxytoluene, C6H3(CH3)(OH)2]. Orcin exposed in succession to the action of ammonia (or putrefied urine) and air, lost its sweet flavor and took on a dark red color (Robiquet, 1829).

Afterwards, several chemists, particularly Stenhouse, studied orcin in detail. According to Stenhouse, the best procedure for obtaining orcin in large scale was to boil the solution obtained by macerating any of the varieties of the Roccella or Lecanora lichen with lime for some hours, and concentrating the liquid by evaporation to about one-fourth its bulk. The excess of lime was then removed by means of a current of CO2 and the filtered liquid evaporated to the consistence of syrup. This residue was then boiled with three to four times its bulk with concentrated alcohol and then left alone to crystallize. The raw crystals were purified by crystallization from an ethereal solution. Repetition of this process produced a highly purified material (Stenhouse, 1848).

According to Luynes, although Stenhouse's process was very effective, it had several shortcomings: In addition to the coloring principle, limewater extracted from the lichens a yellow substance, soluble in acids and bases, which remained mixed with the orcin solution. It was also necessary to use a large volume of liquid, which required a long time to evaporate. Orcin was known to change under the influence of lime and air oxygen; these alterations resulted in the formation of a resinous matter, which made the crystallization of orcein difficult. Luynes found that these inconveniences could be obviated by separating first the active component, erythrite, and then decomposing it with limewater in the absence of air (Luynes, 1863ad).

In a following publication Luynes reported that the density of orcin vapor was 4.20, corresponding to the formula C14H8O4 (= 4 volumes of vapor) (Luynes, 1865a). Most chemists considered orcin to be a substance neutral to coloring reagents, or a glucoside, perhaps an isomer of saligenin (salicyl alcohol). Others believed that it was related to pyrogallic acid, because of their similar chemical behavior. According to Luynes, although orcin was neutral to colored reagents, it behaved sometimes like an acid. For example, adding potassium or sodium carbonate to melted orcin, resulted in effervescence and release of CO2. Mixing an aqueous solution of orcin with another of potassium silicate resulted in the precipitation of silica. An aqueous solution of orcin dissolved a substantial amount of lime; the resulting solution became turbid upon heating and the resulting precipitate redissolved upon cooling. Alcohol produced the same result. Orcin was able to precipitate an acid solution of quinine sulfate and cinchonine sulfate. Nitric acid converted orcin into oxalic acid and a resinous substance. Orcin dissolved in concentrated sulfuric acid producing a solution colored deep violet. Alkalis produced the same reaction. With lime chloride of lime orcin gave a purple-red color, which quickly changed to a deep yellow. With ferric salts it gave a dark red precipitate; it gave no precipitate with normal plumbic acetate, but with basic plumbic acetate a white precipitate was produced (Luynes, 1865a).

According to Luynes, acids did not seem to combine directly with orcin. Luynes overcame this limitation by treating orcin with acid chlorides, such as acetyl chloride. The products of this reaction were orcin diacetate and HCl. Orcin diacetate was a solid, melting at 25 0C, sparingly soluble in water and very soluble in alcohol and ether. Luynes studied also the reaction between orcin with butyryl chloride, benzoyl chloride, succinyl chloride, and chlorine, and the properties of the resulting substances. The results indicated that the behavior of orcin with acids and bases was similar to that of phenol, except for the fact that in the reaction of phenol with acid chlorides the phenol exchanged one equivalent of hydrogen with one equivalent of chloride radical, while orcin fixed two equivalents of acid radical against two equivalents of hydrogen. Hence, orcin should be considered to be equivalent to a diatomic phenol (Luynes, 1865a).

In another publication Luynes discussed the remarkable reaction of orcin with ammonia that under the influence of air and humidity transformed it into the coloring matter named orcein (Luynes, 1865b):

$$C_{14}H_8O_4,2HO + NH_3 + 4O = C_{14}H_9NO_6 + 4OH$$
(orcin) (orcein)

Robiquet had studied some of the circumstances that accompanied this change; he had noticed that the amount of ammonia absorbed during the phenomenon was considerably larger than the amount of air that acted simultaneously, and remarked that it was not known if ammonia participated as such, or through its elements. He also found that at room temperature powdered orcin absorbed ammonia in the same manner as a porous body but released with extreme facility (Robiquet, 1829). Luynes heated a piece of dehydrated orcin in a shallow disk under a bell glass full of ammonia vapor and noted that orcin melted promptly and begun boiling while absorbing rapidly a large amount of ammonia. The same phenomenon took place if dehydrated orcin was maintained melted in a retort while subject to a stream of ammonia gas. In another experiment he dissolved hydrated orcin in cold ether and then bubbled ammonia gas through the solution. The next day he noted that voluminous octahedral crystals covered the flask walls. These crystals were found to contain, by weight, about 11 to 12% of ammonia. The same results were obtained with an ethereal solution of dehydrated orcin. In both cases the crystals were colorless but exposed to air they assumed immediately a violet color (Luynes, 1865b).

Luynes also studied the possibility of using orcin to prepare litmus (tournesol), an indicator for acidity and basicity used since ancient times (Luynes, 1864c). The details of its manufacture were partially known but it seemed the process in use yielded a product little different from the one described in old chemistry books. As mentioned before, it was known that orcin, under the influence of air and ammonia yielded only one violet colored material, the orcein, which did not turn red in the presence of acids. Luynes found that that a slight modification of this procedure led to the formation of a substance having the same properties as tournesol. His procedure consisted in mixing in a retort one part of orcin with twenty-five of crystalline calcium carbonate and five of water containing an amount of ammonia equal to that of orcin. The retort was almost completely sealed and then heated to 600 to 80 0C, for four to five hours, under agitation. The resulting liquor, having a deep violet color, was diluted with water slightly oversaturated with HCl, to precipitate the coloring matter. The latter, washed and dried, was composed of pure litmus. This litmus was sparingly soluble in water and highly soluble in alcohol and ether. The corresponding solutions were colored vinous red, red, and yellow, respectively. The aqueous solution turned onionskin colored in

contact with acids and violet blue with bases. Litmus was insoluble in benzene, carbon disulfide, and turpentine. It dissolved in concentrated sulfuric acid yielding a very rich violet blue solution, which turned red on addition of a large amount of water. Luynes remarked that a dilute alcoholic solution of litmus constituted a highly sensitive reagent for identifying very small amounts of alkaline substances. Dry litmus was very stable and the alcoholic solution was easily and fast prepared (Luynes, 1864c).

Luynes and A. Lionet studied the preparation of compounds in which orcin played the role of an acid (Luynes & Lionet, 1867a). For this purpose they reacted, at an appropriate temperature, crystalline orcin with a mixture of equal amounts of KOH and an alkyl iodide. Their results indicated that operating with an excess of orcin resulted in the formation of an orcin derivative in which one equivalent of hydrogen had been substituted by one equivalent of the alkyl. Thus they prepared methyl, ethyl, and amyl orcin, having formulas C14H7(C2H3)O4, C14H7(C4H5)O4, and C14H7(C10H11)O4, respectively. The first two compounds were liquid and the third one a solid crystallizing as needles. Operating with a mixture of one equivalent of orcin with two of the alkyl iodide and KOH resulted in the formation of diethyl and dipentyl orcin in which two equivalents of hydrogen had been replaced by two equivalents of alkyl: C14H6(C2H3)2O4 and C14H6(C10H11)2O4. Operating in the present of large excess of KOH and alkyl iodide yielded the corresponding trialkyl derivatives C14H5(C2H3)3O4, C14H5(C4H5)3O4, and C14H5(C10H11)3O4 (Luynes & Lionet, 1867a).

Luynes mentioned that orcin was a colorless crystalline substance, which transformed into a violet coloring matter (orcein), under the influence of air and an aqueous solution of ammonia. The simultaneous presence of air and aqueous ammonia was necessary; without water there was no coloration. Luynes had found that pure oxygen or oxidizing agents could replace air in producing the coloration. In addition to orcein, orcin produced two other coloring substances, litmus (tournesol) and a red product. Litmus was prepared exposing to air a mixture of orcin, aqueous ammonia, and sodium carbonate, and the red matter by reacting orcin with vapors of nitric acid (Luynes, 1868b).

Luynes conducted the following experiment: Into a sufficiently large thermometric tube he introduced an aqueous and boiled solution of orcin, together with ammonia and some oxidizing reagents. Afterward, the tube was bent to expel the air and then sealed and heated to 50 °C. A series of tubes was thus prepared, each containing a different oxidant (e.g. potassium permanganate, sodium dichromate, potassium dichromate, and barium dioxide). In every case the oxidant was reduced and the colored matter produced remaining attached to the oxide. With potassium dichromate or ammonia, the solution assumed an intense blue tint similar to the amidochromic salts prepared by Edmond Frémy (1814-1894) (Frémy, 1858). Ammonia copper sulfate was slowly but completely reduced into cuprous oxide. Arsenic acid was likewise reduced and arsenious acid (arsenic trioxide) gave no result (Luynes, 1868b).

In another paper Luynes reported that orcin combined with picric acid in definite proportions, forming a crystalline substance, which in contact with air absorbed humidity becoming totally liquid. This matter was soluble in alcohol and ether and was decomposed by benzene into picric acid and orcin. Chemical analysis indicated that its composition corresponded to the formula C26H11N3O13, that it, it contained an equal number of equivalents of orcin and picric acid (Luynes, 1868c).

Paris blue

In 1861, Persoz, Luynes, and Louis Alphonse Salvétat (1820-1882) announced the discovery of a new dye, which they named Paris blue, resistant to the acids and to light

(Persoz, Luynes & Salvétat, 1861a). They wrote that in 1858 August Wilhelm Hofmann (1818-1892) while studying the action of carbon dichloride on aniline had discovered a new base, to which he assigned the formula C38H17N3 (Hofmann, 1858). During separation of this base from the accompanying impurities he found that the alcohol retained in solution a substance of a magnificent crimson color. This discovery led Persoz, Luynes, and Salvétat to study the possible relation existing between Hofmann's crimson substance and fuchsine (acid fuchsin, magenta), the red dye discovered by the Lyon silk dyers and chemical manufacturers Renard frères et Franc (Renard, 1859). Their results indicated that the only thing common to both substances was the color; their physical and chemical and chemical behavior were completely different. For example, fuchsine was completely soluble in alkalis, behaving like a true acid; it combined with ammonia, KOH, barium hydroxide, etc., forming soluble combinations. The solutions, treated with acetic acid, served to dye the purest shades. This property allowed Persoz, Luynes, and Salvétat to extract their new dye from all the commercial varieties of acid fuchsin, using Hofmann's procedure (Persoz, Luynes, & Salvétat, 1861a).

Thus, in their first experiments, they reacted aniline with carbon dichloride and obtained a viscous oil, which from which the base solidified gradually into a crystalline structure. Purification of the base with alcohol left an alcoholic crimsoned residue. In the second series of experiments they followed the same procedure except using the reagents to prepare fuchsine (tin dichloride and aniline). For this purpose they heated a mixture of 9 g of tin dichloride with 16 g of aniline in a sealed tube, for 30 hours at about 180 0C, and found that the resulting product, instead of being red or violet, was a very bright and pure blue, and required only to be treated with water to dye animal fibers in beautiful brilliant tints. They named this blue Paris blue and assumed that it was another addition to the series of rich colors derived from aniline (Persoz, Luynes, & Salvétat, 1861a).

In a following publication Persoz, Luynes, and Salvétat provided more details about the synthesis of Paris blue (Persoz, Luynes, & Salvétat, 1861b). On breaking the reaction tube, they found a viscous black mass, which diluted in boiling water turned dark blue. The filtered solution, mixed with sodium chloride, precipitated the blue substance and left a dark green liquor. The precipitate was dissolved in water and reprecipitated with sodium chloride. This operation was repeated until the liquid lost completely its green color. The final blue precipitate, after being washed with dilute HCl and water, was dissolved in hot alcohol; upon cooling the blue dye precipitated as brilliant needles. The crystals were soluble in water, alcohol, methanol, and acetic acid, and insoluble in ether and carbon disulfide. They decomposed by heating, yielding violet vapors. The dye was completely destroyed by chlorine; it dissolved in sulfuric acid yielding an amber solution, and dissolved in an alcoholic solution of sulfuric acid producing a blue liquid (Persoz, Luynes, & Salvétat, 1861b).

Persoz, Luynes, and Salvétat published a booklet summarizing their work about dyes (Persoz, Luynes, & Salvétat 1860).

BIBLIOGRAPHIC REFERENCES

Anonymous (2018). France. Archives Nationales. Base Léonore, dossiers nominatifs des personnes nommées ou promues dans l'Ordre de la Légion d'Honneur.

Berthelot, M. (1854). Mémoire sur les Combinaisons de la Glycérine avec les Acides et sur la Synthèse des Principes Immédiats des Graisses des Animaux. *Ann. Chim. Phys*. [3], *41*, 216-319.

Berthelot, M. (1856). Sur la Mannite. *Comptes Rendus, 42*, 1111-1114.

Berthelot, M., Luynes, V. & Sainte-Claire Deville, H. (1866). *Leçons de Chimie Professées en* 1864 *et* 1865. Hachette, Paris.

Dumas, J.-B. & Péligot, E. (1834). Sur un Nouvelle Alcool et ces Dérivés. *J. Pharm., 20*, 548-549.

Dumas, J.-B. & Péligot, E. (1836). Recherches sur la Nature de l'Éthal, Tendant a Prouver que c'est un Corps Analogue à l'Alcool. *Ann. Chim. Phys., 62*, 5-22.

Emptoz, G. (1994). Notice sur Victor de Luynes - Les Professeurs du Conservatoire National des Arts et Métiers. Dictionnaire Biographique 1794-1955; sous la direction de Claudine Fontanon et André Grelon. Paris, vol II, 151-158.

Faraday, M. (1825). On New Compounds of Carbon and Hydrogen and on Certain other Products Obtained During the Decomposition of Oil by Heat. *Phil. Trans.*, *115*, 440-467.

Frémy, E. (1858). Recherches sur les Sels de Chrome. *Compt. Rendus, 47*, 893-890.

Hofmann, A. W. (1858). Faits pour Servir à l'Histoire des Bases Organiques. *Ann. Chim. Phys*. [3], *54*, 197-218, 356-362.

Lamy, A. (1857). Note sur la Phycite, Matière Sucrée du *Protococcus Vulgaris* (Phycée), et sur son Identité avec Érythroglucine de M. Stenhouse. *Ann. Chim. Phys*. [3], *51*, 232-242.

Liebig, J. (1857). Darstellung der Pyrogallussäure. *Liebig Annalen. 101*, 47-50.

Luynes, V. (1857a). Note sur la Formation de l'Arsénite d'Ammoniaque. *Comptes Rendus, 44*, 1353-1354.

Luynes, V. (1857b). Note sur quelques Propriétés de l'Acide Arsénieux. *Comptes Rendus, 44*, 1354-1355.

Luynes, V. (1860). Note sur une Combinaison du Chlorure d'Arsenic et d'Alcool. *Comptes Rendus. 50*, 831-831.

Luynes, V. (1862a). Sur la Constitution de l'Érythrite. *Compt. Rendus, 55*, 624-625.

Luynes, V. (1862b). Extraction du Bismuth de ses Alliages. *Bull. Soc. d'Encour*. [2], *9*, 649-651.

Luynes, V. (1863a). Sur la Préparation Industrielle de l'Orcine. *Bull. Soc. Encour., 62*, 270-275.

Luynes, V. (1863b). Nouvelles Observations dur l'Érythrite. *Compt. Rendus, 56*, 803-804.

Luynes, V. (1863c). Sur le Butylène. *Compt. Rendus, 56*, 1175-1177.

Luynes, V. (1863d). Recherches sur l'Orcine. *Compt. Rendus, 57*, 161-163.

Luynes, V. (1864a). *Recherches sur l'Érythrite et ses Dérivés.* Thèse de physique présentées à la Faculté des Sciences de Paris le samedi 23 juillet, pour obtenir le grade de docteur ès sciences physiques; published as a booklet by Gauthier-Villars, Paris; *Ann. Chim. Phys*. [4], *2*, 385-429; *J. Pharm., 46,* 421-426.

Luynes, V. (1864b). Sur l'Iodhydrate et l'Hydrate de Butylène. *Compt. Rendus, 58*, 1089-1091.

Luynes, V. (1864c). Sur la Préparation du Tournesol. *Compt. Rendus, 59*, 49-51.

Luynes, V. (1864d). Sur le Rôle que Joue l'Érythrite dans les Principes Immédiats de Certain Lichens. *Compt. Rendus, 59*, 81-84.

Luynes, V. (1864e). Sur la Réduction de l'Érythrite par l'Acide Iodihydrique. *Bull. Soc. Chim.* [2], *1*, 11-13.

Luynes, V. (1864f). Sur la Solidification du Butylène. *Bull. Soc. Chim.* [2], *1*, 166-167.

Luynes, V. (1865a). Recherches sur l'Orcine. *Compt. Rendus, 60*, 920-922; *Ann. Chim. Phys*. [4], *6*, 184-203.

Luynes, V. (1865b). Sur l'Action Réciproque de l'Orcine et de l'Ammoniaque. *Comptes Rendus, 60*, 1033-1034; *Bull. Soc. Philom., 2*, 94.

Luynes, V. (1868a). *Notice sur les Travaux Scientifiques de M. Victor de Luynes*. Gauthier-Villars, Paris.

Luynes, V. (1868b). Sur les Matières Colorantes Dérivées de l'Orcine. *Comptes Rendus, 67*, 239-241.

Luynes, V. (1868c). Sur quelques Combinaisons Nouvelles de l'Orcine. *Compt. Rendus, 57*, 656-658.

Luynes, V. (1869). De la Diffusion des Corps. *J. Pharm., 9*, 139-146, 191-201.

Luynes, V. (1872a). Sur l'Acide Borique. *Bull. Soc. Philom., 8*, 91-93.

Luynes, V. (1872b). Sur les Larmes Bataviques. *Bull. Soc. Philom., 8*, 95-96.

Luynes, V. (1873). Sur la Trempe du Verre, et en Particulier, sur les Larmes Bataviques. *Comptes Rendus. 76*, 346-349; *Ann. Chim. Phys*. [4], *30*, 289-302.

Luynes, V. (1875). Sur l'Acide Borique Fondu et sur sa Trempe. *Compt. Rendus, 81*, 80-81.

Luynes, V. (1877). Notes sur Certains Altérations du Verre. *Compt. Rendus, 84*, 303-305.

Luynes V. (1882). *Rapport sur la Céramique*. Imprimerie Nationale, Paris.

Luynes, V. & Esperandieu, G. (1865). Sur la Préparation et quelques Propriétés de l'Acide Gallique. *Compt. Rendus, 61*, 487-490.

Luynes, V. & Esperandieu, G. (1867). Sur la Préparation et quelques Propriétés de l'Acide Gallique. *Ann. Chim. Phys.* [4], *12*, 116-121.

Luynes, V. & Feil, C. (1875). Recherches sur le Verre Trempé. *Compt. Rendus, 81*, 341-344.

Luynes, V. & Girard, A. (1875). Note sur le Pouvoir Rotatoire du Sucre Cristallisable et sur la Prise d'Essai des Sucres Soumis à l'Analyse Polarimétrique. *Compt. Rendus, 80*, 1354-1357.

Luynes, V. & Lionet, A. (1867a). Sur les Dérivés Méthyliques, Éthyliques, et Amyliques de l'Orcine. *Compt. Rendus, 65*, 213-215.

Luynes, V. & Salet, G. (1864). Sur L'Emploi de l'Acide Iodhydrique en Chimie Organique. *Bull. Soc. Chim.* [2], *1*, 166.

Pasteur, L. (1848). Recherches sur le Chloride Arsénieux et sur quelques Arsénites. *J. Pharm*. [3], *13*, 395-400.

Pelouze, J. (1833). Mémoire sur le Tannin et les Acides Gallique, Pyrogallique, Ellagique et Métagallique. *Ann. Chim. Phys*., *54*, 337-365.

Persoz, J. F., Luynes, V. & Salvétat, A. L. (1861a). Faits pour Servir à l'Histoire de l'Aniline; Production d'une Nouvelle Matière Tinctoriale Bleue, le Bleu de Paris. *Compt. Rendus, 55*, 624-625.

Persoz, J. F., Luynes, V. & Salvétat, A. L. (1861b). Nouvelles Observations sur le Bleue de Paris. *Compt. Rendus, 52*, 700-702.

Persoz, J. F., Luynes, V. & Salvétat, A. L. (1861c). *Recherches sur les Matières Tinctoriales Dérivées de l'Aniline*. Bourdier, Paris.

Renard, Fréres. (1859). *Improvements in the Preparation of Red Dyes*. British Patent No 921,12th April 1859 sealed 7th October.

Robiquet, P. J. (1829). Essai Analytique des Lichens de l'Orseille. *Ann. Chim. Phys*. [2], *42*, 236-257.

Stenhouse, J. (1843). On Pyrogallic Acid and some of the Astringent Substances, which Yield it. *Phil. Mag.* [3], *22*, 279-283.

Stenhouse, J. (1848). Examination of the Proximate Principles of Some of the Lichens. *Phil. Trans.*, *138*, 63-90.

Stenhouse, J. (1862). Additional Observations on the Proximate Principles of the Lichens. *Proc. Roy. Soc., 12*, 263-268.

Winter, J. (1909). Notice sur Victor de Luynes. *Bull. Soc. Philom., 7*, 137-147.

Würtz, C. (1856). Sur le Glycol ou Alcool Diatomique. *Compt. Rendus, 43*, 199-204.