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REVIEW ARTICLE

FAUSTINO JOVITA MALAGUTI

Sugar, substitution theory, and amides

FAUSTINO JOVITA MALAGUTI

Azúcar, teoría de sustitución y amidas.

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ABSTRACT

Faustino Jovita Malaguti (1802-1878), an Italian-French pharmacist, proved that diluted, even very diluted acids, at temperatures below 95 ^{0}C, acted in an identical manner upon sugar and that the final result was a mixture of ulmic and formic acid or only ulmic acid, depending if the reaction was conducted in the presence or absence of atmospheric air. Malaguti studied the preparation of mucic and paramucic acid and their derivatives, ethyl citrate and the formula of citric acid, crystalline camphoric acid by the prolonged action of nitric acid on camphor, the preparation and properties of several derivatives of camphoric acid, studied the chlorination of a large number of ethers to prove that the assumption of the substitution theory that one atom of hydrogen could be replaced by one atom of chlorine. His results helped establish the substitution theory and dethrone the chemical theory of Berzelius. Malaguti prepared a large number of pure amides and discovered many new ones, among them mucamide, pyrotartramide, pimelamide, and adipamide. He demonstrated that cystine contained sulfur, carried on the synthesis of pigments for porcelain, the chloroesters and amides of a large number of organic acids, the reciprocal relations between soluble and insoluble salts, the effect of passage of sunlight through different liquids, etc.

Keywords: amides chlorination; citric acid; camphor; substitution; sugar

RESUMEN

Faustino Jovita Malaguti (1802-1878), un farmacéutico italiano-francés, demostró que los ácidos diluidos o muy diluidos, a temperaturas bajo 95 ^{0}C, actuaban de la misma manera sobre el azúcar y que el resultado final era una mezcla de ácidos úlmico y fórmico, dependiendo si la reacción se llevaba a cabo en presencia o ausencia del aire atmosférico. Malaguti estudió la preparación de los ácidos múcico y paramúcico y sus derivados, el citrato de etilo y la fórmula del ácido cítrico, el ácido alcanfórico cristalino por la acción prologada del ácido nítrico sobre el alcanfor, la preparación de varios derivados del ácido alcanfórico, estudió la cloración de un gran número de éteres para demostrar la suposición de la teoría de la substitución de que un átomo de hidrógeno podía ser reemplazado por uno de cloro. Sus resultados ayudaron a establecer la teoría de la substitución y a destronar la teoría química de Berzelius. Malaguti preparó un gran número amidas puras y descubrió muchas nuevas, como la mucamida, piro-tartaramida, pimelamida, y la adipamida. Demostró que la cistina contenía azufre, realizó la síntesis de pigmentos para porcelana, los cloro-ésteres y amidas de una variedad de ácidos orgánicos, las relaciones recíprocas entre sales solubles e insolubles, el efecto del paso de la luz a través de líquidos, etc.

Palabras clave: ácido cítrico; alcanfor, amidas; azúcar; cloración; substitución

INTRODUCTION

Life and career (Gaudiano, 2006; Guareschi, 1902)

Faustino Giovita Malaguti (Figure 1) was born in Pragatto di Crespellano, Italy, on February 15, 1802, the third of the nine children of Giuseppe Valerio, a pharmacist, and Anna Medici. When he was seven year old the family moved to Bologna where his father acquired a pharmacy. After receiving his primary and secondary education at the school of the Padri Barnabiti, Malaguti registered at the university to pursue pharmacy studies and at the young age of 16 obtained his diploma for the free practice of the profession. During his studies he worked as assistant pharmacist in the business of his father and in the university medical clinical directed by Giacomo Tommasini, one of the first physicians to promote the use of the smallpox vaccine. After graduation the pontifical authorities appointed him to the Customs service responsible for inspecting imported medicines and drugs. Malaguti participated in the revolutionary movement of 1831, which declared Bologna's independence from the Papal authority and the city becoming the capital of the United Provinces. During this period Malaguti was nominated secretary of Pio Sarti, Police Minister of the provisional government established in Bologna. After the Austrian army suffocated the revolution Malaguti was imprisoned in Venice for some time and then deported to Marseille. In 1833 Malaguti moved to Paris and obtained a position with Théophile-Jules Pelouze (1807-1867) in the laboratory of Joseph-Louis Gay-Lussac (1778-1850) at the École Polytechnique.

His abilities attracted the notice of Adolphe-Théodore Brongniart (1801-1876), the director of the Manufacture Royale de Porcelaine de Sèvres, who in 1835 invited him to work at his research laboratory, in spite of having no knowledge about the subject. During his seven year stay at Sèvres he published a paper about the pink color manufactured in England by a secret process. Malaguti analyzed the material and was able to reproduce it by melting tannic acid with clay and potassium chromate[3] (Malaguti, 1836b), creating a new violet color called universal lacquer. He also published another paper with Brongniart about kaolin for porcelain (Malaguti & Brongniart, 1841). During his period he enrolled at the Sorbonne and in 1839 he obtained his degree of docteur ès sciences, after successfully defending a thesis about the retarding effect exerted by some liquids upon diffuse light (Malaguti, 1839b). In 1840 he adopted the French nationality and a little afterwards married Fanny Megissier, from whom he had one son, Carlo.

In 1840 he won by competition the chair of General Chemistry at the recently created Faculté des Sciences of the Université de Rennes. Some time later the name of the chair was changed to General and Agrarian Chemistry. Malaguti was the first to teach agrarian chemistry in a French provincial University; his textbooks on the subject (e.g. Malaguti, 1853bc, 1855, 1862, 1865) were a tremendous success and were translated to many other languages. At Rennes he served as

Dean of the Faculty of Sciences (1855-1866) and Rector (1866-1873). His numerous publications about the ability of chlorine of substituting hydrogen were a powerful tool for disproving Jöns Jacob Berzelius (1779-1848) electric theory.

Malaguti died in Rennes on April 26, 1878, after suffering from cardiac problems. Malaguti received many honors and awards for his scientific and public work. He was elected corresponding member of the Accademia Benedettina (1840), of the Accademia dei Lincei (1849), of the French Académie de Sciences (1855), and of the Accademia delle Scienze di Bologna (1856); honorary member of the Académie de Turin (1849), member of the Accademia dei Georgofili di Firenze, of the Società Medico-Chirurgica di Bologna, of the French Société de Pharmacie (1835) and of the French Société Philomatique (1840). In 1860 he was appointed Officier of the Légion d'Honneur and in 1873 promoted to Commandeur. In 1866 Vittorio Emanuele appointed him Commendatore dell'Ordine dei SS. Maurizio e Lazzaro.

Scientific contribution

Malaguti wrote about 80 papers, booklets and books in the areas of agriculture, building materials, inorganic, organic, and analytical chemistry, metallurgy, etc. In addition to the subjects discussed below Malaguti studied ozokerite (Malaguti, 1837d), discovered that cystine contained nitrogen (Baudrimont & Malaguti, 1837); studied the preparation of esters and the substitution of hydrogen by chlorine (Malaguti, 1837fgh, 1839a, 1845), the composition of artificial ruby (Malaguti, 1837e); the composition of sodium phosphate (Malaguti, 1842a), organic acids containing chrome (Malaguti 1842b), the action of phosphoric acid upon ammonium salts and its derivatives (Malaguti, 1847), extraction of silver from minerals and seawater (Malaguti & Durocher, 1847, 1849, 1850, 1856, 1859; Malaguti, Durocher, & Sarzeau, 1856); absorption of soluble ulmates by plants (Malaguti, 1852a), etc.

Organic chemistry

Action of acids upon sugar

Malaguti wrote that there was a vast literature regarding the action of acids upon sugar; in every case the information related to a particular acid without providing a general explanation of the phenomenon. For example, nitric acid transformed sugar first into glucaric (saccharic) acid and then into oxalic acid, cold diluted sulfuric acid changed sucrose into glucose, hot sulfuric acid or HCl transformed sucrose into ulmic acid, organic acids allowed sugar to crystallize, even after they had been neutralized, etc. (Malaguti, 1835a).

Malaguti conducted a series of experiments to prove that diluted, even very diluted acids, at temperatures below 95^0C, acted in an identical manner upon sugar and that the final result was a mixture of ulmic and formic acids, or of only ulmic acid, depending if the reaction was conducted in the presence or absence of atmospheric air, respectively.

Malaguti boiled for several hours 4 g of concentrated nitric acid with a solution of 50 g of sugar in 150 g of distilled water and observed that the solution became dark red while precipitating a black matter partly pulverulent and partly crystalline. Separation of the phases indicated the presence of ulmic and formic acids and a substance insoluble in ammonia, which Malaguti named *ulmin*.[1] Replacement of HCl by phosphoric, arsenic, oxalic, tartaric, citric, and glucaric acid yielded the same results; the only difference was the amount of acid required to achieve the same outcome. The most significant result was that the initial amount of acid was also present at the end of the reaction. According to Malaguti, this last result indicated that the acids acted on sugar by their material presence and not by their composition.[**1**] Not only that, if the acid did not participate in the transformation it was necessary to assume that the water or the air did because sugar had been oxidized to formic acid. In order to confirm this hypothesis Malaguti repeated the experience in an apparatus in which the composition of the interior air could be analyzed continuously. The results indicated that no hydrogen was formed and that there was a progressive decrease of oxygen (Malaguti, 1835a).

An elemental analysis of ulmin indicated that it contained, by weight, 57.39% carbon, 4.72% hydrogen, and 37.89% oxygen, corresponding approximately to the formula C_2H_2O, identical to that of ulmic acid (Malaguti was using then the values of the atomic masses accepted at that time). Malaguti reported that an easy procedure for preparing ulmic acid consisted in boiling for 45 minutes a solution of 10 parts sugar, 30 of water, and 1 of concentrated sulfuric acid. The resulting surface scum was ulmic acid with a little ulmin, which could be separated with ammonia (Malaguti, 1835a).

Malaguti concluded as follows: (1) under the influence of heat both dilute organic and inorganic acids acted in the same way upon sugar, transforming it first into grape sugar and then into ulmic acid, and, if atmospheric air was present, into formic acid; (2) when cane sugar was changed into grape sugar, the action of the acids took place even at ordinary temperatures; (3) the smallest quantity of acid acted in the same manner, but more slowly. A less dilute acid acted faster than a more dilute one; (4) dilute acids, under the action of atmospheric air, were unable to transform sugar into formic acid; and (5) the action of alkalis upon sugar was identical with that of acids (Malaguti, 1835a).[2]

Mucic Acid (galactaric acid) and derivatives

In 1780 Carl Wilhelm Scheele (1742-1786) reported that he had isolated a new acid from milk sugar (Scheele, 1780). As described by him, he had poured 12 ounces of diluted nitric acid on 4 ounces of finely ground milk sugar, which was placed in a glass retort provided with a receiver, on a sand bath. When the mixture attained a certain temperature it entered into such a violent ebullition that the retort had to be taken out of the sand and placed upon a table. The mixture continued to boil for a long time, while releasing dark red fumes. Afterwards the liquid was heated again and nitric acid distilled until the mixture assumed a yellow color. After two days, he added another 8 ounces of nitric acid and distilled the liquid again until the yellow color had disappeared. Eventually a white precipitate formed, which he separated by filtration. Initially Scheele assumed that this powder "could be anything except *calx saccharata* because milk always contained calcium, which would also enter into the milk sugar and form a constituent of it." Additional experiments proved that he was wrong: The powder was found to be insoluble in cold water and slightly soluble in boiling water (one part in sixty of water). The soluble part was separated by crystallization and found to be a salt, which dissolved in water producing a sour solution, which reddened litmus paper. Scheele reported the behavior of the acid with fixed and volatile alkalis, earths, and metals. All the resulting earthly salts were insoluble in water (Scheele, 1780). The pertinent acid was initially known as sacchalactic acid to indicate its origin; the name was changed to mucic acid after it was found that all the gums were able to afford it.

In 1835 Malaguti reported that boiling a saturated solution of mucic acid until evaporation, followed by dissolution of the residue in alcohol and spontaneous evaporation of the alcoholic solution, left a white flocculent residue, which could be crystallized by further dissolution in alcohol and evaporation. The resulting crystals corresponded to a molecular modification of mucic acid, which communicated it with new properties, in spite of both acids having the same composition, corresponding to the formula $C_6H_{10}O_8$. For example, its flavor was more acid than

that of mucic acid and the modified mucic acid and its salts were more soluble in water than the corresponding ones from mucic acid. The acid that crystallized from its aqueous solution was completely insoluble in alcohol; boiling the aqueous solution returned the modified form to the original one (mucic acid). Malaguti believed that the modified mucic, which he named *paramucic acid*, was an isomer of mucic acid (Malaguti, 1835b).

Another significant difference was the reaction with mercurous or silver nitrate: An aqueous solution of mucic acid produced immediately a light and abundant white precipitate while that of paramucic acid generated a grainy heavy precipitate that separated neatly from the liquid (Malaguti, 1835b). Malaguti reported that pyrolysis of paramucic acid yielded a substance containing, by weight, 54.10% carbon, 3.88% hydrogen, and 42.02% oxygen, equivalent to that of pyromucic acid (2-furoic acid) containing one equivalent of water. Berzelius had found that rapid evaporation of an aqueous solution of mucic acid resulted in the formation of a soft red matter, very acid and soluble alcohol, which was not mucic acid or malic acid. Malaguti believed that his acid was different from the one reported by Berzelius because its aqueous solution did not evaporate rapidly and did not leave the soft red residue reported by Berzelius (Malaguti, 1835b).

Another work described the preparation and properties of mucic ester (Malaguti, 1836a).[3] This compound was prepared by heating 1 part of mucic acid with 4 of sulfuric acid until the solution became rose-red, then crimson, and finally black (Malaguti believed that these color changes indicated the formation of a compound between the two reagents, probably sulfomucic acid). The final mixture was left in a closed flask for 12 hours in a closed vessel and then mixed with 4 parts of alcohol of specific gravity 0.814 (91% weight alcohol), without cooling. After 24 hours the crystallized mass was strongly shaken up with alcohol and filtered. The separated dirty white crystals were dried and purified by crystallization from boiling alcohol. The pure crystals were transparent, colorless, shaped as right four-sided prisms of specific gravity 1.17 at 20 ^{0}C. Initially they were insipid but then turned bitter. They melted at 158 ^{0}C, giving off a small quantity of brown oil, and solidified in the crystalline form at 135 °C. After cooling to 70 °C they melted at 150 °C and at 170 ^{0}C they blackened and decomposed into alcohol, water, CO_2, pyromucic acid which partly sublimed, a hydrocarbon, and acetic acid, while leaving a carbonaceous residue. The pure crystals were insoluble in ester, sparingly soluble in cold alcohol, and very soluble in boiling alcohol and boiling water (Malaguti, 1836a).

The pure crystals separated from boiling water were somewhat different: They were shaped as right rhombic prisms with two broad and two narrow lateral edges, with specific gravity 1.32 at 20 °C. They melted at 158 °C and solidified at 122 °C; after cooling to 70 °C they melted into an oily liquid at 100 °C and completely at 132°. Except for their different melting behavior, they presented the same chemical reactions as those crystallized from alcohol (Malaguti, 1836a).

An aqueous solution of both crystals decomposed immediately in contact with the hydroxides of calcium, barium, and strontium, precipitating the corresponding mucate. KOH and NaOH decomposed them into alcohol and mucic acid. Dry NH_3 gas did not react with melted mucic ethyl ester but at 170° it produced alcohol, ammonium carbonate, and very aromatic oil, which dissolved slowly in water. Dry chlorine gas did not seem to react with the melted ester but on cooling the liquid solidified in the form of a transparent resin, very soluble in alcohol and not forming any precipitate with silver nitrate. Elemental analysis of this ammonium mucate indicated that it contained, by weight, 29.86% carbon, 6.50% hydrogen, 11.52% nitrogen, and 52.12% oxygen. Malaguti believed that his results indicated that mucic acid was diacid (dicarboxylic) and that the correct formula of free mucic acid and of the acid combined in salts should be $[C_{12}H_8O_7 + H_2O]$ and $C_{12}H_{10}O_8$, respectively (Malaguti, 1836a). Malaguti also described the preparation and properties of the methyl ester of mucic acid (Malaguti, 1836a).

Citric acid ester

The usual method for determining the formula of a compound was through the analysis of its compounds with metallic oxides. Malaguti believed that it had not been proved that a metallic salt released its water of hydration before it began to decompose. The results that had led him to modify the formula of mucic acid suggested that a better procedure for non-volatile acids was through the analysis of their light esters. As an example of this possibility he selected citric acid, for which Justus von Liebig (1803-1883) had suggested the formula C_6H_5O3 (or $C_{12}H_{10}O_6$) while Jean-Baptiste André Dumas (1800-1884) believed it was possibly the mixture of the same two acids, which continuously metamorphosed one into the other (Dumas, 1833; Liebig, 1833; Malaguti, 1836b, 1837a).

Malaguti prepared the ethyl ester of the acid using the procedure suggested by Thenard, which consisted in heating to boiling a mixture of 90 parts of powdered crystallized citric acid with 110 of alcohol of specific density 0.814 (91% per weight alcohol) and 50 of concentrated sulfuric acid, and stopping the process when a very sensible disengagement of sulfuric ether occurred, which happened when about one third of the volume of the alcohol employed had distilled. The residue was removed from the retort and mixed with twice its volume of distilled water. The ester separated immediately and settled at the bottom of the vessel; after separation it was repeatedly washed with cold water, then with a dilute alkaline solution, and finally dissolved in alcohol and cleaned with pure animal charcoal (Malaguti, 1836b, 1837a). Malaguti gave a detailed description of the physical and chemical properties of pure citric ester, among them, that is was a transparent and yellow oily liquid, smelling like olive oil, having a bitter and disagreeable taste, and density 1.142 at 21 ^{0}C. Heated in an open vessel it emitted a very dense vapor, which inflamed on the approach of flame and left a charcoal residue. Heated in a closed vessel it lost its limpidity at about 120 °C, became reddish at 270 °C, and began to boil and decompose at about 283 °C, releasing an oily matter, dilute alcohol, hydrocarbon gases and citric ester, and leaving a charcoal residue. Citric ester was neutral, soluble in ether and in weak alcohol, and slightly soluble in water. Boiled with a solution of KOH or NaOH it decomposed into alcohol and the alkali citrate; ammonia gas or in aqueous solution showed no immediate action (Malaguti, 1836b, 1837a).

Elemental analysis indicated that the ester contained, by weight, 51.00% carbon, 7.29% hydrogen, and 41.71% oxygen, corresponding to the formula $C_{16}H_{14}O_5$. These results corroborated the formula $C_8H_4O_4$ proposed by Berzelius for citric acid (Berzelius, 1832; Malaguti, 1836b, 1837a). In another short notice Malaguti reported the synthesis and properties of the ethyl esters of pyrocitric and pyromucic acids (2-furoic acid) (Malaguti, 1836c).

Camphoric acid and derivatives

Malaguti prepared crystalline camphoric acid by the prolonged action of nitric acid on camphor; elemental analysis by combustion with cupric oxide indicated that it contained by weight, 60.20% carbon, 8.00% hydrogen, and 31.79% oxygen, corresponding to the formula

$C_{20}H_{16}O_4$ or [$C_{20}H_{14}O_3 + H_2O$] (the actual values and formula are 59.98%, 8.06%, 31.96%, and $C_{10}H_{16}O_4$). Boiling camphoric acid with HCl or sulfuric acid produced a bitter syrupy substance, insoluble in water, and soluble in alcohol and alkalis. Treatment of the alkaline solution with acids reprecipitated the original substance, which was found to have the elemental composition 63.40% carbon, 8.86% hydrogen, and 27.74% oxygen, corresponding to the formula $C_{40}H_{28}O_6$, which Malaguti wrote in the form [$C_8H_{10}O + H_2O$], that is, it was equal to two molecules of camphoric acid (each deprived of an equivalent of water), one molecule of ester, and one of water, which was the exact composition of the free vinic acids. Distillation of this syrupy substance, *camphovinic* acid, in a glass retort over a lamp, produced a butyraceous substance, methane, and a carbonaceous residue. The butyraceous matter treated with boiling alcohol and the solution gradually cooled, precipitated very long neutral crystals, without taste and smell, fusing and volatilizing without undergoing decomposition, but combining, notwithstanding their neutrality, with bases, forming crystallized salts. Elemental analysis indicated that the crystals contained 66.24% carbon, 7.70% hydrogen, and 25.86% oxygen, corresponding to the formula $C_{20}H_{14}O_3$, that is, camphoric acid less an equivalent of water. The alcoholic mother liquors, from which the anhydrous camphoric acid was precipitated, afforded a dense oily, which volatilized without decomposition, and with composition 65.88% carbon, 9.43% hydrogen, and 24.69% oxygen, corresponding to the formula $C_{28}H_{24}O_4$, agreeing with camphoric ester [$C_{20}H_{14}O_3 + C_85_{10}O$] (Malaguti, 1836d, 1837b).

Malaguti summarized his results as follows:

Common camphoric acid = $C_{20}H_{14}O_3 + H_2O$

Anhydrous camphoric acid = $C_{20}H_{14}O_3$

Free camphovinic acid = $C_{40}H_{28}O_6 + C_8H_{10}O + H_2O$

Camphoric ester = $C_{20}H_{14}O_3 + C_8H_{10}O$.

In a more extensive paper Malaguti gave a detailed description of the synthesis and properties of the above compounds (Malaguti, 1837c).

Substitution of hydrogen by chlorine

Malaguti studied extensively the chlorination of a large number of esters to prove the basic assumption of the substitution theory that one atom of hydrogen could by replaced by one atom of chlorine in a variety of compounds. For example, he showed that oxalic ether (diethyl oxalate), under the simultaneous action of heat (100 °C), direct light, and chlorine, converted into a crystallized substance, in which all the hydrogen had been driven off and replaced by chlorine, and having for formula C_4O_3, $C_8Cl_{10}O$ [$C_{12}Cl_{10}O_4$]. Here Malaguti is using Berzelius formula for oxalic acid, C_4O_3]. The resulting substance was neutral, had no smell or taste, melted at 170 °C, and froze in rectangular plates. Above 170 °C it began to decompose and could not be distilled; it was decomposed by simple contact with all fluids having an affinity for chlorine (e.g. alcohol, simple and compound esters, essential oils, etc.). Among the numerous products of the decomposition was an oily sweet substance, insoluble in water, neutral, aromatic, and having a composition corresponding to anhydrous *oxalovinic* acid in which all the hydrogen had been replaced by chlorine. Malaguti named so because its structure was similar to that of sulfovinic acid (ethyl sulfate). Addition of ammonia to this oil led to the precipitation of needle-shaped crystals, which were volatile, fusible, and neutral, and whose composition could be represented by oxamethane (ethyl oxamate), because it only contained the two atoms of the hydrogen of the amide; the rest had been replaced by chlorine (Malaguti, 1840a). Malaguti showed that chloroxamethane, under the action of aqueous ammonia, transformed into ammonium chloroxalovinicate. The latter could be used to prepare chloroxalovinic acid, which differed from oxalovinic acid in having chlorine instead of hydrogen (Malaguti, 1840b).

Amides

In 1830 Dumas reported the discovery of a new substance, which he named *oxamide* (Dumas, 1830). He wrote that it was a known fact that treating animal matter with KOH resulted in the release of large amounts of ammonia and that this process was very slow compared with the release of ammonia when treating an ammonium salt with the same base. These facts led him to assume that in animal matter the hydrogen and nitrogen were not combined as ammonia. Dumas found that the distillation of ammonium oxalate generated oxamide, ammonia, ammonium carbonate, water, CO_2, CO, and cyanogen. Oxamide was found to have a curious property: Heated with KOH it produced ammonia and oxalic acid although it did not contain these two substances. Oxamide was a volatile solid, little soluble in cold water, and found two contain, by weight, 26.95% carbon, 4.59% hydrogen, 31.67% nitrogen, and 36.79% oxygen. Dumas believed that many ammonium salts were able to generate substances similar to oxamide and he proposed to consider this substance as the type of a family, which the named *amides* (Dumas, 1830).

Dumas' discovery was followed by the synthesis of a variety of other amides, particularly by chemists who believed that they could be used for a better understanding of alkaloids and neutral nitrogenous vegetable substances. In a letter to Dumas, Malaguti wrote that he had put much effort in preparing large amounts of very pure amides, and at the same time, discovering many new ones, such as mucamide, pyromucamide, pyrotartramide, pimelamide, adipamide, etc. Discovering new amides was an easy task; when you had an acid, you had an ester, and when you had an ester, you had an amide. The only experimental difficulty was preparing highly pure acids (Malaguti, 1846).

Malaguti described some of his experimental results as follows. Contacting for a long time oxamide with an aqueous solution of chlorine, followed by elimination of the excess chlorine by evaporation, resulted in the formation of oxalic acid and no ammonium chloride, showing that chlorine had acted upon oxamide the same as upon an ammonium salt. Boiling one part of oxamide with four parts of concentrated nitric acid resulted in the release of a gas containing 4 volumes of nitrogen, 1 of nitrous oxide, and 2 of CO_2. The same result was obtained when boiling a mixture of one equivalent of ammonium nitrate and one of oxalic acid; the oxygen of the nitric acid oxidized not only the hydrogen of the ammonia but likewise the carbon of the oxalic acid. On the one hand, heating to 220 ^{o}C crystallized ammonium oxalate in a closed tube converted it into ammonium carbonate and CO, without the formation of any oxamide. On the other hand, heating oxamide to 310 °C in a hermetically closed metallic tube converted it immediately into cyanogen, CO and ammonium carbonate. Likewise, heating a mixture of sand and oxamide in a tube from 330 ° to 330 °C, generated only ammonium carbonate, cyanogen and CO (Malaguti, 1846).

According to Malaguti ammonium chloracetate, heated under the same conditions, yielded phosgene, ammonia, and CO. Decomposing chloracetamide at a faint red heat produced a large quantity of gas composed of CO_2, cyanogen chloride, CO, and some phosgene. This reaction had several alternatives: Heating chloracetamide and water in a closed glass tube to above 100 °C produced chloroform and ammonium carbonate without the chloracetamide being previously converted into ammonium chloracetate. Now, if the tube was opened when the temperature reached 130 °C, the chloracetamide was found unaltered, while ammonium chloracetate was already decomposed between 112 ° to 115 °C into chloroform and ammonium carbonate (Malaguti, 1846).

Malaguti also studied the decomposition of mucamide by heat. Mucic ester in contact with aqueous ammonia immediately converted into mucamide. This amide was a white tasteless substance, slightly soluble in boiling water from where it crystallized as microscopic needles of density 1.589 at 13.5 ^{O}C, insoluble in alcohol and ester, and converting into ammonium mucate under the influence of water at 130 °-140 °C. Ammonium mucate heated to 220 °C, became soft and colored, while disengaging CO_2, water, ammonium carbonate, pyromucic acid and a peculiar amide, and leaving a residue of carbon and paracyanogen. The decomposition was complete at 240 °C. Malaguti also described the decomposition of ammonium mucate under a series of conditions, as well as the preparation and properties of pyromucamides and mucovinic acid (Malaguti, 1846).

Optical phenomena

Malaguti wrote that Jean-Baptiste Biot (1774-1862) had observed that certain perfectly transparent solid bodies were able to retard the impressionability of chemical paper prepared with silver nitrate and that this result had led him to investigate if this same property was present in liquids having a well determined composition and being perfectly transparent and colorless. The existence of a property of this nature would be related to the molecular composition of the liquids and be of the same order as the power for deviating the polarization plane of light (Malaguti, 1839b).

The experimental procedure was based on the fact that a paper impregnated with silver chloride (chemical paper) went through a series of shades before becoming black. These nuances were easy to copy with colored paper (benchmark paper), if the photographic paper used was not extremely sensitive. Thus, it was possible to measure the time required for the sensitive material to achieve a certain coloration resulting from the action of light passing through a screen of a given liquid. The chemical paper was prepared by dipping paper in a very diluted alcoholic solution of HCl, followed by drying, plunging in a dilute solution of silver nitrate, and drying in total darkness. The benchmark paper was prepared by tinting it with a mixture of lead carbonate, China ink, and red madder dark lacquer (alizarin), diluted with mucilaginous water. Mixing the components in different proportions allowed obtaining any desired nuance. A rectangular strip of the chemical paper was glued over a sheet of benchmark paper and the whole located within a black chamber. The test was conducted simultaneously with and without the screen of the liquid being tested. Malaguti's paper gave a detailed description of the measurements of the exposition chamber, the disposition of the materials being tested, the operating procedure for measuring the time required for the chemical paper to achieve the nuance desired, and the precautions to be taken in order to perform all the experiments, as much as possible, under equal operating conditions (temperature, pressure, and humidity). Sixteen liquids were tested, among them, distilled water, absolute alcohol, methanol, acetone, ethyl acetate, sulfuric acid, and glacial acetic acid. Malaguti summarized his findings in two tables, one describing the operating conditions for each substance being tested (for example, date, hour of the day, climatic conditions, time required for achieving the nuance, etc.), and another giving the relative time against air assumed to be one. Except for distilled water, all the tested liquids slowed down the required time (Malaguti, 1839b).

Reciprocal action of soluble and insoluble salts

Malaguti first memoir on the subject was related to the reciprocal action between soluble salts (Malaguti, 1852b, 1853a). In the introduction he wrote that Claude-Louis Berthollet (1748-1822) had postulated that "when a neutral salt is dissolved, and when an acid is added to its solution, the latter enters into concurrence with the combined acid; both act on the alkaline base, each in the ratio of its mass, as if the combination had not existed" (Berthollet, 1803). Malaguti understood that the expression "each in the ratio of its mass" implied the idea that the quantity of an acid necessary for performing the division would be so much the greater as the acid was weaker, and if the two acids were equally strong, they would divide the base proportionately to the number of their atoms. Hence, on the one hand, a natural consequence of this principle seemed to be that the decomposition that could take place between two salts, or a saline couple dissolved, so long as nothing was separated (precipitated), had to be so much the greater as the acid and the stronger base were be separated in the two primitive salts (Malaguti, 1852b, 1853a). On the other hand, if it took place *as if the combinations had not existed,* that is to say, as if the acids and bases had been put in contact separately, then the two inverse experiments would give the same result. In other words, "if the quantities of the salts decomposed in two saline couples, containing the same elements, but inversely distributed, were represented by two coefficients, the two coefficients would be complementary" (Malaguti, 1852b, 1853a).

Malaguti tested this hypothesis using the acetates of potassium, sodium, barium, strontium, and lead, the nitrates of potassium, barium, strontium, and lead, and the sulfates and chlorides of potassium, sodium magnesium, manganese, and zinc. For this purpose, he selected pairs of salts which were both soluble in water, but only one of which was soluble in alcohol (salts that decomposed in alcohol were rejected, for example cupric acetate and zinc acetate). These salts were mixed in equivalent proportions in water and then poured into a large quantity of alcohol. If his principle were correct then at least one of the two new salts created would to be completely insoluble in alcohol. Analysis of the precipitate would indicate the mode and measurement of the primitive decomposition. If the mixing process was accompanied by a change in temperature, the analysis was performed after the mixture had returned to the initial temperature (Malaguti, 1852b, 1853a).

Malaguti determined the *direction of decomposition* of a saline couple as follows: Assume that *A* and *B* are the two salts dissolved in water and *A*' and *B*' the two new salts generated in alcohol. The quantity *A*' and *B*' will be equal, smaller, or larger to the quantity of *A* and *B* that will not be decomposed. The correct relation is the one that will determine the decomposition direction of decomposition a saline couple. Similarly, the *coefficient of decomposition* was defined as the atomic (molecular) quantity of the two salts decomposed. For example, if operating with one equivalent of potassium sulfate and one equivalent of sodium acetate resulted in a residual amount of 64% of the potassium sulfate, then the coefficient of decomposition would be 36. Malaguti conducted a total 22 experiences and summarized the results in two tables, one for which the coefficients of decomposition were larger than 50, and the other were the coefficients were less than 50. Inspection of the results indicated that the higher coefficients corresponded in general to the saline couples in which the strongest acid and base were initially *separated* in the two salts, and the lower coefficients belonged to the couples one of which contained the stronger acid *and* base. For example, the coefficients of decomposition of the pairs (potassium chloride - zinc sulfate) and (zinc chloride - potassium sulfate) were 84 and 17.6 respectively. The only exceptions to these rules were the two couples containing nitric acid and acetic acid and the bases of potassium and barium. In addition, the results were independent of the direction in which they were done: Mixing one equivalent of barium acetate with one equivalent of lead nitrate produced the same amounts of barium nitrate and lead nitrate as when one equivalent of barium nitrate was mixed with one equivalent of lead acetate (Malaguti, 1852b, 1853b).

The next paper was related to the mutual decomposition of soluble and insoluble salts (Malaguti, 1857). In a brief introduction Malaguti wrote that Pierre-Louis Dulong (1785-1838) had written one of the first papers on the subject, which unfortunately was very limited in scope: it only described the action of sodium and potassium carbonates (or bicarbonates) on the insoluble salts (Dulong, 1803). Dulong's experiments involved boiling for an hour or so a solution of the alkali carbonate mixed with the insoluble salt finely reduced. The results indicated that the sodium and potassium bicarbonates were never completely decomposed by any insoluble salt. In addition, all salts that had ammonia as their base were completely decomposed by insoluble carbonates; the new insoluble salt replaced the decomposed carbonate and ammonium carbonate became disengaged as it was formed. When the soluble salt had an insoluble base the decomposition continued until the liquid contained nothing more in solution (Dulong, 1803). Years later, Heinrich Rose (1795-1864) confirmed Dulong's findings (Rose, 1855).

In an extensive memoir about the extraction of silver, Malaguti and the geologist Joseph-Marie Élisabeth Durocher (1817-1860) reported that many substances assumed to be insoluble, decomposed mutually after their particles had been in contact for a long time in the presence of water. For example, mashed cadmium sulfur in contact with silver chloride or mercurous chloride generated cadmium chloride and mercurous sulfide or silver sulfide. The same results were obtained with cupric sulfide or tin disulfide. If silver chloride was dissolved in sodium hyposulfite (thiosulfate) or ammonia, it was decomposed almost immediately by all the sulfides, sulfoarsenides, and arsenides. Another interesting result concerned the phenomena observed when boiling a solution of a salt containing a suspension of an insoluble salt, when both salts did not have a common element. Three results were possible: (1) no interaction took place; (2) a complete decomposition occurred, and (3) there was a partial decomposition. In the first situation, the reverse reaction occurred with total decomposition; in the second case, there was no decomposition, and in the third, there was partial decomposition (Malaguti & Durocher, 1850).

Malaguti conducted a large number of experiments using compounds having different coefficients of decomposition and concluded as follows: (1) the reciprocal interaction between soluble and insoluble salts showed little difference with the one between soluble salts; (b) in most cases where the resulting coefficients of decomposition of saline pairs having the same principles but inversely distributed, were not mutually complementary, the result was due to insolubility or adherence of the particles; (c) the principal cause limiting the decomposition of a saline pair was the mutual action between the new salts generated by the decomposition; and (d) the results of the mutual decomposition of insoluble salts and soluble ones were simply a particular case of a natural law stating that during the interaction between two molecular systems their elements tended to generate new systems in a stable state (today: minimizing the total value of the Gibbs function) (Malaguti, 1857).

Fig. 1: Faustino Giovita Malaguti (1802-1878)

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