Contribution of Chevreul to lipid chemistry

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Abstract – Michel Eugène Chevreul entered at 17 the laboratory of Vauquelin, at the Museum. He began his investigations on animal fats in 1811. They appear as yet the most complete and the best executed experiments found in all chemistry. For the first time, he combined fractional solution, crystallization, distillation, melting point determination, and ultimate analysis. All started with the isolation of an acid and solid substance, “margaric acid”, the first of a long list of fatty acids isolated from various fats. Studying saponification, he determined that “anhydrous glycerine” was combining with water. After studying human gallstones, he discovered “cholesterine” (cholesterol). From whale spermaceti, he described “cetin” (mainly cetyl palmitate), containing no glycerol. He isolated from sheep fat a new acid he named “stearic acid”. This component was proposed in a joint patent by Chevreul and Gay-Lussac (1825) for the fabrication of very efficient candles. He discovered several volatile fatty acids in cow and goat butter (from C4 to C10). His master work (Recherches chimiques sur les corps gras d’origine animale, 1823b) contains his experimental procedures and his theoretical conclusions on the nature of fats, it may be considered as the first treatise on lipochemistry.

Keywords: Chevreul / fats / fatty acids / cholesterol / saponification

1 Chevreul’s life

He was born in 1786 in the town of Angers, where his father and grandfather were surgeons. After 4 years of schooling at the central school of Angers, he moved to Paris. At the age of 17 he entered the service of Louis Nicolas Vauquelin, 26 years older. Attracted by studies in chemistry, he was taking courses at the College de France and became rapidly the assistant of Vauquelin, professor of applied chemistry at the Museum. After 10 years of brilliant research on lipids (1813–1823), he was appointed at the age of 38 (until the age of 97) director of dyeing at the Manufacture Royale des tapisseries des Gobelins. During this time he was elected member of the Academy of Sciences (at 40), appointed professor of organic chemistry at the museum (at 44) and then director of this institution. He made his last communication to the Academy of Sciences one year before his death, in 1889, 5 months before his 103rd birthday.

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Chevreul’s life was entirely devoted to work. He lived near constantly between the Museum, the Gobelins, the Agricultural Society and the Institute. Towards the end of his life, he claimed to be the dean of the students and he liked to say that he had known during a century 4 kings, 2 emperors, 3 republics and 4 revolutions. He said that the secret of his longevity was to never smoke, to never eat fish, to drink water and chocolate but no wine or milk.

2 Chevreul’s scientific work

The scientific work of Chevreul was very prolific and in very different fields as with most 19th century scientists. A book published for its centenary has listed 500 publications, communications, notes and books.

During the first 5 years in Paris (1807–1813), under the direction of Vauquelin, he investigated mainly on the coloring principles of plants. It is interesting to note that in addition he isolated a sugar from the urine of diabetic patients, which he identified as equivalent to grape sugar (glucose). During this short period, he published 27 scientific notes. During the following 10 years (1813–1823), he studied only fat chemistry. In 1813, he published his first paper on the chemistry of soap made from pork fat. This paper may be considered as the birth of lipochemistry. He then published 6 important communications on the chemistry of lipids. In 1815, he published the chemical composition of gallstones and described the presence of a new fatty substance, cholesterol.

In 1823, he published a book that brings together all his results on lipids: “Recherches chimiques sur les corps gras d’origine animale” (Chevreul, 1823b). In this famous book, Chevreul established the foundation of lipochemistry.

From 1824 to 1883, as director of dyeing at the Gobelins he devoted himself almost entirely to research on plant dyes. He has done 14 important publications in this field. The milestones are two books: “Leçons de chimie appliquée à la teinture” and especially his masterwork “De la loi du contraste simultané des couleurs”.

Apart from the previous domains, Chevreul has written several publications on criticism, analysis and discussion of books or articles from other European scientists, articles on magic, archaeology, education, hygiene, mineralogy, horticulture and agronomy.

3 State of organic chemistry and knowledge about lipids before Chevreul’s work

From the Middle Ages to the beginning of the 19th century, “organic bodies” were limited to those from the living world, it was believed that their existence required the intervention of a “vital force” inaccessible to science. Only a few organic substances were known, such as wine alcohol, acid from ants, sugar from some plants, soap, the sweet principle of oils. They remained mysterious because there was no way to purify and analyze them. The medical chemist Claude-Louis Berthollet (1748–1822) recognized at the end of the 18th century “that it was time to rid chemistry of the obstacles which slow down its progress and to introduce into it a true spirit of analysis”. He discovered that nitrogen was a real principle of natural substances. Thanks to Antoine Laurent Lavoisier (1743–1794) who may be undoubtedly considered as the father of modern chemistry (he named oxygen and nitrogen) and Berthollet, chemists were able to know and measure 4 main elements (C, H, O, N) that make up living organisms.

In the field of lipids, we can get an idea of their knowledge in reading the treatise on chemistry published in 1794 by Antoine François Fourcroy (1755–1809). He said about fat: “we only know the action of fire, air and some reagents on this substance”. Furthermore, he divided all fatty substances into fixed oil, volatile oils and fats.

Lavoisier has shown that oils were composed of hydrogen and carbon. He believed that solid fats like wax could contain oxygen, which gave a state of solidity. In 1774, he wrote in his laboratory notebook “What is oil? It seems that by combustion, it can be reduced to air, but we know nothing beyond”. Chemists observed that after distillation fat gives various products including a light oil called “oil of the philosophers”.

The formation of soaps proved that the oil is acidic since it combines with the alkalis (theory of Berthollet, born 38 years before Chevreul).

In 1783, Carl Wilhelm Scheele (1742–1786), 44 years older than Chevreul, discovered the “sweet principle of oil”, currently recognized as glycerol, by boiling olive oil with lead oxide.

4 Scientific training of Chevreul

Who are the masters who trained and guided Chevreul? Fourcroy and especially Vauquelin.

Vauquelin was a pharmacist but also a great chemist, skilled in mineralogy and chemical analysis. He discovered chromium and beryllium and isolated nicotine, urea from urine and asparagine (the first amino acid discovered). He was the first chemist to separate biological materials into fats, proteins, starch and sugar. In the field of lipids, Vauquelin wrote in 1811 a thesis entitled “On the analysis of cerebral matter, considered in man and in animals” which earned him both the doctorate and the chair of professor of chemistry at the faculty of medicine (Vauquelin, 1811). He described the presence of phosphorus in brain lipids extracted by alcohol but unfortunately he did not continue in this way. Therefore, he missed the discovery of phospholipids!

Vauquelin taught Chevreul the use of the most important instruments for analysis in organic chemistry: the precision scale and the device designed by Lavoisier for elemental analysis. This analysis was based on the gravimetric determination of specific adsorbent materials before and after selective flue gas adsorption.

5 Chevreul’s work on lipids

His main work concerns the saponification of fatty substances and the products of this chemical reaction. Compared to his predecessors, he used a combination of new methods to obtain precise elemental analysis based on that saponification but also on the solubility in solvents, crystallization, measurement of the melting point, distillation and fractionation of salts. All of these methods are described in detail in his famous book on lipids published in 1823 (Chevreul, 1823b). Chevreul’s fame is currently based on the
scientific study of fat saponification, a reaction processed by man for centuries but whose the correct mechanism has just been discovered for the first time in organic chemistry.

Historians teach us that soap was known and used since at least 2500 years among the Sumerians. The Romans made great use of it. Berthollet was the first chemist to be interested by the mechanism of saponification. He believed that fatty substances were acidic and that they united with bases. Scheele had no idea despite his discovery of the formation of glycerol ("sweet principle") during the reaction.

Curiously, Chevreul’s interest in saponification and composition of oils and fats came from Vauquelin who gave him a sample of pork fat to analyze. It was also reported that Chevreul observed salt crystals after leaving accidentally soapy water evaporated overnight in some glassware. He raised the question: what is the origin of that salt? Through deductive reasoning, he realized it must be the result of the soap. When he learned how soap was made by mixing animal or vegetable fat with alkali in water, he was surprised because there was no salt in that process either.

The first results of his research on saponification will be published in 1813 (Chevreul, 1813a).

In this first paper, Chevreul reported that, by diluting soap from pork fat in water, a portion dissolved and another deposited in small and pearly crystals. After decomposing this substance with an acid he prepared a solid fatty substance with acidic properties and melting at about 56°C. He named it “margarin” and later “margaric acid” (pearl in greek). He thought it was a pure substance but it was a mixture of palmitic (mp 64°C) and stearic acid (mp 72°C). Later, he isolated and purified stearic acid after several steps of dissolution and precipitation and determined its exact elemental composition.

These experiments were the origin of the concept of “fatty acid” which was developed when later he isolated several other fatty acids from various fats. Thanks to these new results, this paper written at the age of 27 may be considered as the first to open the field of lipid chemistry.

The originality of the methods used by Chevreul comes from the combination of several techniques such as saponification followed by repeated chemical and physical treatments. This new methodology has hardly changed since then.

In a second paper, also published in 1813 (Chevreul, 1813b), he reported that the portion of the soap dissolved in water contained a second acidic product, a liquid, which he named “fluid fat”, later named “oleic acid”. Thus, he has shown that the potash soaps consisted of two different soaps, formed by the union of potash with two different fatty acids. He announced also that he was able, after Scheele, to isolate the “sweet principle of oil” in the water phase and to determine its elemental composition, very close to that currently known. He named it “glycerine” (Greek: glykeros, sweet, now glycerol) and concluded that fat is a combination of anhydride of glycerol with an organic acid. Carefully, he hypothesized that in fats, glycerol played the same role as alcohol (ethanol) in ethyl acetate. Berthollet confirmed this hypothesis carrying out the synthesis of glycerides (Berthollet, 1854). The chemical formula for glycerol was only determined one year later by the famous French chemist Charles Wurtz (1855).

Chevreul concluded that, during saponification, the alkali displaced the anhydride, which combined with water to form glycerol, and the acid part of the fat combined with the alkali to form a salt, that is to say a soap.

The third contribution, published in 1815, was devoted to the saponification process (Chevreul, 1815a). First, Chevreul examined whether oxygen was necessary for the reaction. He demonstrated that a successful saponification is obtained when running the process in the absence of air. Thus, he disproved the theory of Fourcroy that oxygen took part in the reaction. Furthermore, as an important precision for the saponification reaction, he confirmed the participation of water by determining the carbon, hydrogen, and oxygen in the original fat and in the saponification products (glycerol and fatty acids). Thus, by elemental analysis, he demonstrated that the total weight of these products was about 5% higher than that of the initial fat, proving that water was necessary to the saponification process. A short time later, he analyzed samples of fats from several animal species. He discovered that sheep or beef tallow contained a new fatty acid with a fusion point higher than that of margaric acid, which he named stearic acid.

The recognition of the importance of the constancy of melting point to control the purity of a chemical species is due to Chevreul. In his general chemistry course, Gay-Lussac wrote: “Chevreul was the first to demonstrate this proof for fatty substances – thus the melting point of fatty stearic acid is +70°C and margaric acid +60°C”.

His chemical studies led him to invent the stearic candle – approximately our current candle – which definitively replaced the tallow candle in 1825 (Chevreul took out a patent for the stearic candle with his chemist friend Gay Lussac). It must be noticed that this patent brought him nothing, as usually happens, only the industrialist had the exclusive profit of the invention. An anecdote: the banquet of 1000 seats offered by the city of Paris for the 100th anniversary of Chevreul’s was entirely lit by candles offered by the manufacturer at the time.

In the field of fatty acids, Chevreul studied also the composition of cow and goat butter (Chevreul, 1823a). He discovered by repeated crystallisation of fatty acid baryum salts that these fats contained volatile acids (now short-chain fatty acids). He referred to these compounds as butyric acid (C4), caproic acid (C6) and capric acid (C10) after determining their composition. Iso-valeric acid (C5) was determined in delphin oil (first “delphinic acid” and later “phocenic acid”). Anecdotically, he reported in 1861 the presence of butyric acid in the fruit of Ginkgo biloba (Chevreul, 1861), which explained their smell of rancid butter.

In 1816, Chevreul examined the composition of fats from animals other than pig (i.e., man, sheep, beef, jaguar and goose) (Chevreul, 1816). He found that all fats could be resolved into two principles: a solid one, “stearine”, containing stearic acid and a liquid one, he named “elaine” (later olein), containing oleic acid. Furthermore, he decided that the difference in physical properties of the examined fats depended on the different proportions of these principles. It must be emphasized that these conclusions remained unchanged until the knowledge that glycerol possessed a triple alcoholic function in 1850 (Berthelot and Wurtz) and the synthesis of fat principles (glycerides) by Berthelot in 1854. Our knowledge of fat structure in terms of fatty acids was far more recently greatly extended, thanks to the efforts of Thomas Hilditch who revealed in 1964 that all natural fats were composed largely of mixed triacylglycerols.
In 1817, Chevreul published a memoir in three parts describing the composition of spermaceti (Chevreul, 1817a) and dolphin oil (Chevreul, 1817b, c).

Spermaceti is found in the head cavities of the sperm whale (and, in smaller quantities, in the oils of other whales). The name spermaceti comes from the close resemblance of this semi-liquid waxy substance to semen. It assists in the whale buoyancy and echolocation. About 2000 L of spermaceti may be collected from one head. This substance was highly demanded back in the 19th and 20th centuries for making candles, lamp oil, lubricant and cosmetic products. Given these uses, the sperm whale was decimated until 1982, when its hunting was definitively prohibited.

After several chemists (Fourcroy, Pouillet de la Salle), Chevreul was interested by the fatty content of biliary calculi (or gallstones). He showed that the main compound (a "crystallised substance") was not saponifiable. He named this new lipidic substance "cholesterine" (from the Greek chole = bile and stereo = solid) which he considered as "an immediate principle". He determined with a great precision its elemental composition and its fusion point: 137°C. Chevreul published his main results in the Annales de Chimie in 1815 (Chevreul, 1815b), later he demonstrated the presence of cholesterol in the bile of human (Chevreul, 1824a).

It was the first proof of the existence of an unsaponifiable lipid. Far later, the correct molecular formula of cholesterol was proposed by an Austrian chemist, Friedrich Reinitzer (1888), and the exact structure was established by Otto Rosenberg and Harold King from the University of London (1932), more than a century after the discovery of Chevreul. For the anecdote, Reinitzer discovered the properties of liquid cholesterol, and salt fractionation; his experiment was proposed by an Austrian chemist, Friedrich Reinitzer (1932), more than a century after the discovery of Chevreul. He determined with a great precision its elemental composition and its fusion point: 137°C. Chevreul published his main results in the Annales de Chimie in 1815 (Chevreul, 1815b), later he demonstrated the presence of cholesterol in the bile of human (Chevreul, 1824a).

The sixth chapter is a summary and a series of conjectures on the immediate components of fats.

In this key book, Chevreul proposed for the first time a classification of all lipids known at his time, a classification that could still be used considering fatty acids, glycerides, waxes and cholesterol. Thus, he separated fats into two divisions: the acid and non-acid fats. The first was divided into volatile (short-chain fatty acids) and non-volatile fats (long-chain fatty acids) and the second one into four groups: cholesteraline, cetine (cetyl alcohol), glycerides with long-chain fatty acids and glycerides with short-chain fatty acids.

Considering the content of his book, Chevreul presented for the first time a model of a complete set of research in lipid chemistry. Furthermore, admitting that Chevreul may be considered as the father of lipochemistry, he may be also the father of the whole organic chemistry.

Following the achievement of his main research on fats, he wrote in 1824 a voluminous treatise on organic analysis, "Considérations générales sur l’analyse organique et sur ses applications" (Chevreul, 1824b). In this book, he presented for the first time a clear and accurate account of the methods of immediate analysis, which must necessarily precede an ultimate analysis of fats but also of all organic compounds. After discussing the difficulties, he examined the effects of dry heat and the influence of oxygen. He gave indications on the use of various solvents, acids, bases and salts. He explained also the possible applications of immediate organic analysis on arts, medicine, zoology and botanics.

In 1850, while Chevreul, as director of dyeing at the Gobelins, was entirely devoted to the study of colors, he wrote a long paper describing experimental research on oil paint (Chevreul, 1850). Besides several investigations on the role of various metals and the importance of the substrate, he examined the mechanism of the desiccation of paint based on linseed oil. After several experiments, he concluded that: "The experiments which I am about to report demonstrate that paint dries by absorbing oxygen, so that a plank of oak wood which has just been painted dries faster in a bell jar filled with oxygen than it would have had done in atmospheric air; they show, moreover, that it could not have dried in a bell jar filled with carbonic acid". Furthermore, he demonstrated that the drying of oil is accelerated by the presence of lead and manganese oxides. He reported that the action of these metallic soaps is linked to the metal and not to the fatty acids, which constitute them. The fixation of oxygen by walnut oil had already been noticed in 1804 by the Swiss chemist Nicolas-Théodore de Saussure (1804) but in comparison with this simple observation Chevreul gave a host of practical details and measurements for paint users based on numerous experiments.

6 Conclusion

Chevreul’s contemporaries would later write that he was "the Lavoisier of organic chemistry because he was able to unravel the chaos of this complex and obscure science".
The famous German chemist Julius Liebig will say that “his classic works are the keystone of all that has been done, for forty years, in organic chemistry”.

The great Swedish chemist Berzelius wrote that his investigation was the most complete and the best executed series of experiments yet found in all of chemistry. He asserted that Chevreul’s work ought to serve as a model for young scientists who wished to do research in any field of chemistry.

The main criticism, which could be made, is that his very precise investigations were purely analytical, thus resembling the work of naturalists describing living species. It must be noticed that the Chevreul’s work was mainly experimental and that it was widely used later by other chemists even during his lifetime to establish the basis and mechanisms of many reactions in organic chemistry.

Finally, it seems appropriate to quote a sentence pronounced by the president of the Academy of Sciences in a short tribute six days after the announcement of the Chevreul’s death, he said: “When Mister Chevreul named himself the Dean of the students of France, he taught us that, in science, there is always something to learn and that any individual who stops is soon overtaken by his emulators or his successors”.

References


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