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Gustave-Clément Fleury's Work on Plant Growth and Vegetable Principles in the Nineteenth Century

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Abstract

Gustave-Clément Fleury (1833–1910) was a French pharmacist who studied the process of germination in a group of seeds having a high content of fatty matter (castor bean, rapeseed, sweet almonds, and spurge) and tried to determine their role in the embryo state. He found that the fatty material not only furnished respiratory matter during germination but also yielded new materials that the plant needed for its growth. Fatty matter transformed first into dextrin and then into organized cellulose. The oxygen of the air burned the excess of carbon and hydrogen present in the fat and in the resinous matter and brought them into the composition of the pertinent carbohydrates. A given weight of oily seeds always acquired oxygen in the course of germination. Fleury determined the composition and properties of a large variety of natural products, among them, white agaric, *Polyporus officinalis*, common guava, silky oak and gutta-percha. He also developed an efficient method for determining the amount of morphine in opium and studied the simultaneous fermentation of grape sugar to determine if it was possible to force it simultaneously into glucose and fructose. He also studied the inversion of sugar by means of acids and their salts, and determined the mathematical relations between the variables of the process.

Key words: Agaric, Germination, Guava, Morphine, Sugars.

1. Introduction

Plant growth and vegetable principles have attracted the attention of human beings since the beginning of history. Both concepts have played a vital role in the development of agriculture and natural medicine. Their knowledge and understanding developed very slowly; for many centuries they were strictly black boxes and all advances were based on trial and error. In the nineteenth century better experiments allowed obtaining a more scientific understanding of the basic phenomena.

2. Plant Growth

2.1 Germination

Several notable scientists, such as Jean Ingenhousz (1730–1799), Jean Baptiste Van Mons (1765–1852), Theodore Saussure (1767–1845), Jean Baptiste Boussingault (1802–1887), and Gustave-Clément Fleury (1833–1910) (Fig.1 & Appendix), studied the physiology of germination and proposed explanations. Saussure was one of the pioneers in the elucidation of the phenomenon (Saussure, 1799). Most scientists agreed that seeds put in contact with water and pure nitrogen (or

Fig. 1. Gustave-Clément Fleury (1833–1910)

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pure hydrogen) did not germinate; CO_2 was produced and its mixture with the nitrogen resulted in an increase in the volume of the atmosphere of the plant. If the nitrogen was replaced by oxygen, CO_2 was also produced but now the atmosphere of the plant was reduced while oxygen was absorbed. Formation of sugar during germination was also an effect of the presence of oxygen. The seed absorbed oxygen and employed it partly to form CO_2 with its carbon. According to Saussure there were three possibilities: (1) the amount of CO_2 formed was less than the amount of oxygen absorbed by the seed. This meant that the seed absorbed part of the oxygen for internal purposes and part to form CO_2 with its carbon; (2) the amount of CO_2 formed was larger than the amount of oxygen absorbed by the seed. Here it was necessary to accept that the seed produced CO_2 independently of the gas formed by combination with the oxygen of the atmosphere; and (3) the amount of oxygen that disappeared was identical with that present in the CO_2 formed during germination. This meant that the oxygen was absorbed only to form CO_2 with the carbon of the seed. No experiments had been carried to discern between these three alternatives. Saussure carried four delicate eudiometric experiments; in one of them he put 21 seeds weighing 3 grams over a wet sponge and the whole was put in a vessel containing 267 cm^3 of atmospheric air that had been washed with limewater. After eight days the seed had germinated and produced rootles, and the volume of the air inside the vessel had decreased 1/13th of its primitive volume, to 248 cm^3. All the calculations proved clearly that a corresponding volume of CO_2 had replaced the oxygen consumed (Saussure, 1799). Analysis of the composition of wheat seeds, before and after germination, are shown in Table 1 (Saussure 1833).

Table 1. Wheat seeds analysis, before and after germination.

	Germination	
	Before	After
Starch	72.72	65.8
Gluten	11.75	7.64
Dextrin (gluten)	3.46	7.91
Sugar (gluten)	2.44	5.97
Albumen	1.43	2.67
Residue	5.5	5.6
Total	97.3	97.69

In another set of experiments, Saussure proved that this conclusion was invalid in the case of oleaginous seeds, characterized by the presence of a large amount of oil and absence of starch, for example, hemp (*Cannabis sativa*), colza (*Brassica oleracea*, L.), and Chilean tarweed (*Madia Sativa*, DC.). The results also indicated that the germination of oleaginous seeds was accompanied by the production of sugar and partial destruction of their oil, as shown in Table 2 for 100 g of colza (Saussure, 1842):

Table 2. Colza seed analysis (100 g).

	Germination	
	Before	After
Oil	40.7	36.9
Sugar	9.8	10.3
Mucilage	7.2	7.3

The doctoral thesis of Fleury consisted in a chemical study of the process of germination in order to clarify certain poorly known aspects of this phenomenon (Fleury, 1864b, 1865). For this purpose he restricted his work to a group of seeds known for their high content of fatty matter (castor bean, rapeseed, sweet almonds, and spurge) and tried to determine their role in the embryo state of the vegetable. He believed that the nature and amount of the gases released during the process might offer an answer to the question; unfortunately the amount of gas released was too small to perform a eudiometric analysis. For this reason he designed his own apparatus, which he believed allowed the separation and analysis of

the gases with a minimal error. Fleury's equipment consisted essentially of three sections; The first one absorbed air from the laboratory and eliminated its CO_2 and humidity by means of three tubes in series, containing, respectively, pumice stone saturated with concentrated sulphuric acid (to eliminate most of the humidity and organic substances), a solution of KOH of density 1.27, and pieces of KOH (to eliminate the CO_2). The clean air was then fed to a glass bell adhered to a plate, varnished inside and outside and containing the seeds to germinate. This flask was carefully and hermetically sealed to avoid the entrance of atmospheric air or leakage of the internal gas. The water necessary for the germination was contained in a flask located inside the glass bell. A water pump aspired the internal gas first through a tube containing sulphuric acid and then through three U tubes containing calcium chloride. A Liebig condenser containing a solution of KOH, and two additional tubes containing solid KOH and calcium chloride followed. This part of the circuit ended with a battery of tubes holding a known weight of KOH (to determine the amount of CO_2 released during germination), red hot cupric oxide (to burn the combustible matter), sulphuric acid (to absorb water and ammonia), and a known weight of KOH (to absorb CO_2); their respective increase in weight signalled the presence of hydrogen, CO, and hydrocarbon. Fleury gave a detailed description of the precautions he had taken to eliminate the possibility of contamination by the external air, the possible leakage of the gases produced, full combustion of the hydrocarbon gases, as well as calibration of the apparatus (Fleury, 1864b, 1865).

The seeds were sown in a sand bed (previously washed with HCl and then calcined) located on top of the base plate of the glass bell. During the germination process the seeds were kept out of the influence of light, to avoid the growth of green matter and the partial decomposition of the CO_2 formed. Fleury remarked that a large number of seeds did not germinate, probably due to tight agglomeration or poor quality; the decomposition of these seeds affected the analysis of the true gases released. This result forced him to make an elemental analysis of the seeds employed.

His first series of experiments was done with 10.921 g of castor oil seeds during a germination period of 37 days. He reported the amounts of CO_2 produced directly, as well as the water and CO_2 produced by the combustion of the gas. His results indicated that the amount of CO_2 produced increased continuously, substantiating the results of other researchers. The production of CO_2 increased until a certain stage of the formation of green matter, which reduced the amount of CO_2 by converting it into other materials required for growth (respiration). The total amount of water produced by combustion was 0.1455, corresponding to 0.01616 of hydrogen. Fleury speculated if this hydrogen had been released combined with carbon or as free gas accompanied by CO. This question was very hard to answer; the simplest hydrocarbon was methane, which contained hydrogen and carbon in the ratio 1:2 (Fleury assumed that hydrogen was a monatomic element, as believed in his time); in this situation about 1/12 of the hydrogen would be in a free state (Fleury, 1864b, 1865).

In the second part of his work Fleury studied the chemical changes experienced by oleo substances during germination (Fleury, 1864, 1865). The initial step involved determination of the immediate composition of the seeds. A certain weight of seeds was dried at 110 ^{0}C to constant weight and part of it separated for further elemental analysis. The amount of fatty material was determined by extraction with carbon disulphide and evaporating the extract to dryness. The residue of the extraction process was treated with aqueous tartaric acid to coagulate the albuminous matter and the filtrate boiled with HCl to transform the gum and glucose into dextrin. The resulting solution was then titrated with a solution

of KOH and cupric tartrate. The amount of cellulose present was determined by a similar analytical procedure. The mineral substances present were determined by a standard procedure. For example, Fleury found that the seeds of castor had the composition (% weight) given in Table 3.

Table 3. Composition of Castor seeds (% weight).

Water	6.18
Mineral matter	3.10
Albuminous matter	20.20
Sugar and similar compounds (without starch)	2.21
Fatty and resinous substances	46.60
Cellulose	17.99
Undetermined substances	3.12
Total	100.00

The next step was the germination of the raw seeds using the procedure described before and including their analysis at given germination periods. The results as given in Table 4 were obtained, for example, with colza seeds.

Fleury provided similar tables for the other fatty seeds studied, and reached the following conclusions: (a) The fatty material present in the seed not only furnished respiratory matter during germination but also yielded new materials, which the plant required for its growth; (b) it seemed that the first transformation of the fat was into sugar or dextrin, which then became organized into cellulose. This process involved the loss of one or two equivalents of water. This stage sometimes occurred so rapidly that it was difficult to determine the preceding change; (c) the oxygen of the air only burned the excess of carbon and hydrogen present in the fat and resinous matter to bring them to the composition of the pertinent carbohydrates (dextrin, sugar, and cellulose), but sometimes it went further and became fixed on the fatty matter. A given weight of oily seeds always acquired oxygen in the course of germination. This absorption was specific to the vegetable transformation studied in oily seeds; (d) fatty matter disappeared more rapidly from germinating seeds than from the bodies of starving animals; (e) the hourly amount of CO_2 produced during germination was lower than the one disengaged during the respiration of birds and small mammals, and was larger than that for animals weighing one kilo or more; and (f) it was not necessary to look for any catalytic agent susceptible of causing the transformations; the play of chemical affinities under vital influence was sufficient to account for the changes (Fleury, 1864b, 1865).

2.2 Fruit ripening

Saussure also studied the action of green fruits on atmospheric acid (Saussure, 1822). Initially he believed that they produced the same effects as the leaves; they released oxygen by decomposition of CO_2, with the difference that in an equal volume, they decomposed much less. His experiments indicated that grapes in the state of verjuice, and

Table 4. Colza seed analysis at given germination period.

Time, days	Fatty material	Sugar and analogues	Cellulose	Albuminoidal matter
0	46.60	2.21	17.99	20.20
6	45.90	*	*	*
11	41.63	*	*	*
16	33.15	9.95	*	*
21	7.90	18.47	*	*
26	10.30	17.72	*	*
31	10.18	26.90	29.99	20.31

the green fruit of the Jerusalem cherry (*Solanum pseudocapsicum*), exposed to the sun, and adhering to the plant and soil, which made them grow, added oxygen to the air in the vessel in which they were enclosed, while the same fruit destroyed the oxygen of the vessel when it contained limewater. Saussure found that the disengagement of oxygen was less when the fruits were detached from the plant that bore them. Like the leaves, they absorbed oxygen in the dark, replacing it in a volume equal to the fruit, by an equal volume of CO_2. When in the sun they decomposed only in part the CO_2 produced during the night, while on the plant they decomposed it altogether. This partial and purely accidental difference depended evidently on the decay or loss of the vegetative force that the fruit suffered when detached from its plant and received no nourishment (Saussure, 1822). Saussure concluded that green fruits in sunshine and darkness, had the same influence on the air as the leaves, only less intensively; during the night the green fruit caused the disappearance of the oxygen of their atmosphere, and replaced it by CO_2, which they partially absorbed; during their exposure to the sun the green fruits disengaged, completely or partially, the CO_2 they absorbed during the night; green fruits, detached from the plant and exposed to the successive action of the light of the sun, changed the air little or nothing in purity and volume; and the ability of green fruit to decompose CO_2 decreased as they ripened (Saussure, 1822).

Fleury inspected the ripening process of dates at the beginning of autumn (Fleury, 1877a). Initially the fruits were soft and viscous and had a clear sweet taste; most of them still had the peduncle attached. After two or three months their aspect changed completely, they were dry and covered by an abundant efflorescence of glucose and their taste was now less agreeable and quite similar to that of manna. Water extraction yielded a solution that was precipitated by lead sub-acetate. Fleury eliminated the excess of sub-acetate with lead carbonate and found that the remaining solution contained cane sugar and reducing sugar in the ratio 0.05, against a ratio of 1 in the fresh fruit. In other words, during the ripening process the cane sugar was transformed almost completely into reducing sugar. Fleury also looked into the possibility that the process also involved the formation of glucose or inverted sugar. He did not have a polarimeter, for this reason he analysed the solution with the cupro-potassium (Fehling) reagent and also with a solution of mercury iodide and potassium iodide. The results indicated the presence of inverted sugar. This sugar bleached an acid solution of potassium permanganate and promptly transformed into glucose. Fleury added that the dates he had examined were unripen at the time of their collection and that the dates sold in Algiers kept their normal colour and flavour. Hence, the cane sugar of dates that was isolated from the influence of vegetative forces slowly changed into inverted sugar (Fleury, 1877a).

3. Natural products

3.1 White agaric

Fleury published two papers about the composition of white agaric (*Boletus laricis*, now *Polyporus officinalis*), a gilled mushroom (Fleury, 1870, 1875a). He extracted the dry and pulverized fungus with dry ether and obtained a ruby red extract, which deposited a white gelatinous substance. Evaporation of the total mass left a solid residue corresponding to 57.87% by weight of the total initial material. This residue seemed to be composed of two different substances, which Fleury named *white agaric resin* and *agaricic acid*, which were easily separated by common solvents. Fleury carried the separation by distillation in the presence of alcohol (Fleury, 1870).

The agaric resin was red brown when in bulk and fair when powdered; it was very soluble in ether yielding a very viscous solution, soluble in

methanol, ethanol, chloroform, and acetic acid, and insoluble in benzene and carbon disulphide. Their solutions did crystallise but yielded spherical amorphous globules melting at 89.7 ^{0}C. The resin was easily dissolved by ammonia and diluted KOH, producing highly coloured solutions, and was precipitated by cold alcohol and most metallic salts. An elemental analysis indicated that the resin contained, by weight, 71.93% carbon, 9.58% hydrogen, and 19.46% oxygen, corresponding to the formula $C_{51}H_{32}O_{10}$ (C = 6; O = 8; H = 1). The resin tasted bitter and acted as a purgative with doses of 0.15 g (Fleury, 1870).

Agaricic acid appeared as white microscopic needles grouped as beams with a melting point at 145.7 ^{0}C. Heated a few degrees below its melting point it lost water and assumed a yellow colour, without volatilization. It was soluble in concentrated alcohol, less in chloroform, and slightly soluble in acetic acid, benzene, and carbon disulphide. In alcoholic solution, when distilled, it volatilized with the alcoholic vapour. Its sodium salt was precipitated by alcohol; with diluted solutions of metallic salts it gave generally crystalline precipitates. Elemental analysis indicated that agaricic acid contained, by weight, 63.44% carbon, 9.75% hydrogen, and 26.81% oxygen (Fleury, 1870).

In his second paper Fleury reported a more detailed analysis of the composition of the mushroom *Polyporus officinalis* (Fleury, 1875a). He now extracted 500 g of the powdered fungus with dry ether and obtained a solution that was initially red and then colourless. The separation of the resin from the crystalline agaricic acid was performed by successive extractions with ether, alcohol, cold and boiling water, water acidulated with HCl, and with an aqueous solution of NaOH. The sodium agaricate separated as a cheese-like precipitate, which agglomerated by agitation into a plastic mass, which was hard to wash. Further dissolutions in water and precipitation from alcohol resulted in crystallization of the salt as translucent prisms. Fleury neutralized the acid with several bases, analysed the corresponding salts, and found no agreement between the results of the analysis and the amount of base employed. The best approach to accuracy suggested that the equivalent number of the acid was 224 and its formula $C_{24}H_{44}O_7$ (today $C_{24}H_{40}O_7$). Treatment with very dilute sulphuric acid produced a substance, which reduced the cupro-potassium liquor suggesting the possibility that it was glucose. Fleury found that the addition of the elements of water to the resin represented the composition of the agaricic acid, and that agaricic acid amounted to about one-fifth of the weight of the fungus (Fleury, 1875a).

Extraction of the fungus with alcohol yielded a strongly red solution, apparently due to the air; evaporation of the same left a residue with a consistency of hard wax, from which ether dissolved a resinous body soluble in alkaline liquids. This wax was acidic, not crystallizable, and contained 1.5% of nitrogen, by weight. It combined with metallic oxides. The fraction insoluble in ether behaved like a resin; it was reddish, contained nitrogen and melted below 100 ^{0}C. It formed viscous solutions with alkalis and gelatinous precipitates with other bases. Extraction of the mushroom with cold water yielded a red solution, which on concentration deposited microscopic crystals of calcium oxalate (and possibly also magnesium oxalate); the remaining solution contained a brown body, resinous, highly nitrogenated and acidic, which reduced the cupro-potassium liquor (Fleury, 1875a).

Fleury also reported the results of extracting the mushroom with boiling water; water acidulated with HCl, and alkaline (KOH) water. His results indicated that 100 g of the mushroom contained the substances (grams) as given in Table 5.

Fleury observed that the amount of resin was surprisingly high leading to the question how the respiratory action was carried during the life of the mushroom (Fleury, 1875a).

Table 5. Composition of the mushroom, weight %.

Water	9.200
Resin soluble in ether, and agaric acid	60.584
Resin with magnesium sulphate	7.282
Resinous body with calcium and magnesium salts	2.514
Nitrogenous substance with salts	1.900
Oxalate, malate, and phosphate of calcium, magnesium and iron	1.058
Nitrogenous substance soluble in KOH	7.776
Residue	9.686
Total	100.000

3.2 Common guava (*Psidium guajava*)

Fleury studied the composition of the bark and leaves of common guava, at the request of a physician who used them as the basis of many prescriptions (Fleury, 1878). His results indicated that no alkaloid was present in these structures. A detailed analysis of the bark indicated that it contained, by weight, the substances as given in Table 6.

Table 6. Composition of the bark, weight %.

Water	5.900
Tannin	12.100
Water soluble substances (sugar, etc.)	13.800
Resin and chlorophyll	1.726
Cellulose	34.126
Calcium oxalate	30.770
Other salts	1.578

Fleury pointed to the high content of calcium oxalate in the bark. He tried many methods for dosing the tannins and succeeded only as follows:

A certain amount of the substance was extracted with alcohol of 90^0C and the solution was evaporated and dried in a stove. An identical weight was triturated in the presence of magnesium hydrate and a little amount of water; the resulting mixture was dried in a capsule and extracted with alcohol of 90^0C and the extract evaporated to dryness. The difference between the original amount and this residue represented, more or less, the weight of tannin contained in the vegetable matter (Fleury, 1878).

3.3 Silky oak (*Grevillea robusta*)

Fleury wrote that the trunk of the silky oak, a tree that had been acclimated in Algiers, presented frequently an exudation similar to the one appearing on cherry trees, which did not seem to affect the surrounding vegetation (Fleury, 1884a). He decided to examine this product in detail. The exudation was brown, little transparent, and somewhat sturdy. It slightly swelled in contact with water producing a white persistent emulsion, which passed all the filters. Its microscopic examination did not show the presence of starch and the emulsion did not colour an iodine solution. Upon calcination it left 3% of cinder containing mostly calcium carbonate and a small amount of potassium salts. Grounded and extracted with alcohol it deposited an abundant deposit easily separated by filtration. This precipitate was the true gum. Evaporation of the alcoholic extract left a fluid reddish resin, corresponding to about 5.6% of the weight of original raw resin; it was transparent, odourless, and practically non-volatile, soluble in diluted alkalis, methanol, and carbon disulphide, and behaved like a weak acid. The pure resin was greyish, swelling a little in water and turning it viscous. The mixture did not seem to be a true solution; it hardly passed a filter and became turbid. It was not precipitated by ferric chloride but upon addition of a small quantity of potassium hydroxide or carbonate it dissolved easily and the resulting solution was precipitated by ferric chloride. This feature differentiated it from all the known gums. The alkaline solution was levorotatory and did not react with the cupro-potassium liquor. Nitric acid transformed it into mucic acid mixed with a little of oxalic acid. Boiling it for several hours with dilute sulphuric acid changed it into a reducing sugar having

rotatory power +94, which could not be separated from dextrin but was very similar to Senegal (Arabic) gum (Fleury, 1884a).

3.4 Gutta-percha

Fleury mentioned that from a surgical viewpoint, *gutta-percha* presented the inconvenience of yielding brittle apparatuses. In warm climates such as Algiers, it became so brittle after a few months that did not allow its use in surgery. Fleury found that a mixture of nine parts of gutta-percha with one of camphor yielded a product exempt of all these inconveniences; it was soft and joined perfectly with itself at 58 ^{0}C. Cooled down it remained coherent and elastic, making it extremely useful for surgical uses (Fleury, 1881).

3.5 Dosage of tannin

Fleury wrote that some chemists had suggested dosing tannin by absorbing it from its solutions by means of violin strings made from the tunic of the small intestine of the sheep; unfortunately this material was hard to obtain. For this reason he looked for alternative organic matter (Fleury, 1892). An appropriate substance seemed to be white of eggs after it had hardened. He crushed it to a fine powder in a deep mortar and then washed the product with a 10% solution of alcohol in water, slightly acidulated with tartaric acid (to saturate the alkali of the albumen). The solution was evaporated to dryness and the albuminous residue used to dosage tannin as follows:

The liquid containing tannin was mixed with a known amount of the albuminous material, equivalent to seven or eight times the assumed weight of tannin. The mixture was left for eight hours, with frequent agitation, to let the absorption occur. It was important to verify that the liquor was acidic and not alkaline. The remaining liquor was tested with ferric chloride to verify that all the tannin had been absorbed. The solid phase was separated by filtration, washed with a dilute solution of alcohol in water, dried at 100 ^{0}C, and weighed. A sample of the albuminous residue was dried under the same conditions, to determine its water content. The difference between the two proportional weights indicated the weight of tannin absorbed. Fleury warned that the tannin of the nutgall should not be dosed by this procedure because its absorption seemed to be incomplete or too slow (Fleury, 1892).

3.6 Alkaloids

Fleury believed that the existent methods for determining the amount of morphine in opium left much to be desired, they were lengthy and very expensive, independently if they were used for instructional or commercial purposes (Fleury, 1867). It was of interest to simplify the manipulations and the amount of opium required. As a result of his experiments he developed a new method, which satisfied these goals:

Two grams of opium were cut in thin strips and macerated in a stoppered flask with 8 cm^3 of water containing about 15 drops of ammonium oxalate, intended to decompose the possible calcium meconate present, which affected the procedure. The mixture was then crushed in a mortar and filtered. The solid retained was washed several times with water and the liquors mixed with an equal volume of alcohol of 80-85% and with enough aqueous ammonia to keep the odour. The resulting solution was put in a stoppered bottle and left alone for 24 hours to precipitate the morphine. The liquid was filtered, the crystals washed with alcohol of 40% and then dissolved with an excess of a titrated solution of oxalic acid. The presence of an excess of this reagent was detected by adding two drops of a tincture bark of Saint-Marthe (*Cœsalpinia echinata*), which turned yellow in the presence of an excess of oxalic acid. The amount of excess was determined by titration with NaOH. This procedure allowed determining amounts of morphine of about 0.1 g within 1 mg (Fleury, 1867).

In another publication Fleury criticized the procedure proposed by Cornelius Oudemans (1825–1906) for determining the amount of alkaloid by optical means. He gave some numerical examples showing the errors in the results when examining samples containing two or more alkaloids (Oudemans, 1884; Fleury, 1884b).

Fleury observed that there was no agreement regarding the possible influence of quinine salts on the formation of mould in different organic matters (Fleury, 1874). In order to clarify this matter he performed the following experiments, using quinine hydrochloride and three different substrates: (1) a highly diluted solution of monosodium tartrate, (2) a solution of sodium acetate, and (3) a solution of tannin acidulated with HCl. The vases containing these mixtures were covered with a tissue and left, close one to the other, in a room were the atmospheric temperature varied between 20^0 and 25 ^{0}C. After 12 days the first vase presented abundant cryptogamic vegetation similar to the one that grew over pure monosodium tartrate, signalling that the alkaloid was inactive. After 33 days the contents of the second vase remained unchanged; after mixing it with acetic acid it remained unchanged for an additional 34 days showing that the quinine salt could act as anti-parasite in neutral and acid media. This was an interesting result because it was known that acid solutions of quinine sulphate developed promptly a growth of microscopic champignons (against the no action observed with quinine acetate). In this situation sulphuric acid acted in the same manner as phosphoric acid and phosphates acts in the putrefaction process, providing sulphur to the tissue of the fungus. After 33 days the contents of the third vase were exempt of organized vegetable products; its tannin presented the same reactions as the original compound. This result showed that the quinine salt was able to protect a quite alterable principle, such as tannin (Fleury, 1874).

3.7 Sugars

Fleury wrote that during the alcoholic fermentation of a mixture of glucose and fructose the glucose was transformed first, a phenomenon that had not been tested with grape juice (Fleury, 1868a). It was important to know if under the complex conditions for vinification it was possible to force the simultaneous attack of both sugars. For this purpose he carried the following experiments:

He mixed 50 cm^3 of a two-year Muscat wine that had not begun to ferment, with lead sub-acetate, eliminated its excess with hydrogen sulphide, and let the mixture evaporate in the presence of sulphuric acid and calcium oxide. Once the volume had decreased to its half, Fleury measured its deviation with a Soleil polarimeter and found it to be -112.5^0, at 29 ^{0}C in a tube 22 cm long. He also tested the liquid with the Fehling reagent and found that 100 cm^3 contained 26.116 g of reducing sugar. These results indicated that one litre of the wine examined contained 131.88 g of sugar material and that the ratio of fructose to glucose was 2.20. He repeated this experiment using a seven-year old Grenache wine and found that one litre of it contained 106.8 g of sugar material, mostly fructose. These results showed that grape wine followed the general results of alcoholic fermentation (Fleury, 1868a).

In another work he studied the inversion of cane sugar by means of acids and their salts (Fleury, 1875c, 1876a). It was known that at room temperature the reaction of an acid with sugar was slow enough to be followed stepwise; the system remained homogenous all the time and the amount of acid remained constant. Thus it was expected that the elementary action of the affinities would manifest itself without complications and it would be possible to study the effect of the products of the splitting of cane sugar (glucose and fructose) upon the rate of the reaction. No experimental evidence existed about the possible recombination

of the glucose and fructose back into cane sugar. If it existed, it would manifest itself in slowing down the reaction (Fleury, 1875c, 1876a). Fleury conducted his experiments as follows:

He used cane sugar containing only traces of glucose, which he purified by alcohol washes. Two grams of this sugar were put in a gauged flask and mixed with the acid and salt to be studied and enough water to fill the flask to its capacity (100 cm^3). For very long reactions, a small drop of creosote was added to avoid the formation of mould or other reactions. The liquid was then put in several glass test tubes of 20 cm^3 capacities to carry simultaneous experiments at a constant temperature. The progress of the reaction was followed with a Soleil sacharimeter. The initial solutions contained 16.9 g of sugar per 100 cm^3 of water and marked 100^0 in the sacharimeter. For each acid or salt, Fleury reported his results in a table and graph, giving the time of reaction, the amount of acid or salt added per 7 g of sugar, the percentage of sugar converted, and the temperature. The acids employed were sulphuric, HCl, phosphoric, and arsenic (H_3AsO_6), and the salts potassium bisulphate, aluminium sulphate, and ammonium sulphate. Fleury found that his results were well represented by the following formula:

$$I - y = \left[kf(a)\right]^{x}$$

where I is the amount of initial sugar, x the time of reaction, y the proportion of sugar transformed, k a coefficient dependent on the temperature and nature of the acid employed, a the amount of acid employed, and $f(a)$ a function of the proportion of acid, undetermined from the experiments. Fleury remarked that his equation predicted that the reaction was complete at an infinite period of time and also, that there was no recombination of the glucose and fructose. He also reported that the reaction mixture contained potassium bisulfide partially decomposed (Fleury, 1875c, 1876a).

Appendix

Gustave-Clément Fleury was born on December 30, 1833, in Chenay, department of Deux-Sèvres, France, the son of Joseph Auguste Fleury, a Sargent in the police, and Marie Virginie Suvaget. In 1855, after completing his basic classical studies, he entered the military service as an assistant pharmacist and four years later was awarded his degree of pharmacist first class from the École Supérieure de Pharmacy in Strasbourg, after defending successfully a thesis about pharmaceutical and chemical synthesis (Fleury, 1857). Afterwards he was admitted as a pharmacist trainee in the Val-de Grâce military hospital in Paris (Barillé, 1910; Anonymous, 2017). In 1859 he participated in the Italian campaign (fought by the Second French Empire and the Kingdom of Sardinia against the Austrian Empire) with the rank of aide-major pharmacist. In 1863 he won by competition a post of répétiteur at the École du Service de Santé Militaries of Strasbourg and a year later he was awarded his doctoral degree from the Faculty of Sciences of Strasbourg, after reading a thesis about the chemical aspects of germination (Fleury, 1864b). In 1866 he won a post of adjunct professor of medical chemistry and physics at the Écoles Supérieures de Pharmacie of Strasbourg, after defending a thesis about the heat effects accompanying chemical reactions (Fleury, 1866). Between 1870 and 1876 he served as adjunct professor of chemistry applied to hygiene at the École d'Application of Vale-du Grâce, while serving in the army as pharmacien-major and chief of the pharmaceutical services (Barillé, 1910; Anonymous, 2017). Fleury participated in the campaigns of the French army in Africa serving as chief pharmacist in the Hospital of the King in Algiers. In 1889 he was appointed by the Minister of Public Instruction to the chair of pharmacy and toxicology at the École de Médicine et Pharmacie of Nantes, replacing Ambroise Andouard (1839–1914), a position he kept until his retirement in 1903. Fleury was corresponding member of the Société de Pharmacie (1876) and of the Académie de Médicine (1893), and chevalier of the Légion de Honneur (1886). Gustave Fleury passed away at Talence (Bordeaux) on July 18, 1910 (Barillé, 1910; Anonymous, 2017).

Bibliography

Anonymous. Base Léonore, dossiers nominatifs des Personnes nommées ou promues dans l'Ordre de la Légion d'Honneur, Archives Nationales France, 2019.

Barillé, A. Le Professeur G Fleury, *Bulletin Sciences de Pharmacie*, 17 (1910): 671–674.

Fleury, G C. Recherches Chimiques sur la Germination, Thèse de chimie présentée à la Faculté des Sciences

de Strasbourg le 21 Mai 1864 pour obtenir le grade de docteur ès- sciences, Silbermann, Strasbourg, 1864b.

Fleury, G C. Recherches Chimiques sur la Germination, *Annales de Chimie et Physique*, 4.4 (1865):39–65.

Fleury, G C. Essai des Opiums, *Journal de Pharmacie*, 4.6(1867):99–102.

Fleury, G C. Sur le Sucre des Vins, *Journal de Pharmacie,* 4.8 (1868a):323–325.

Fleury, G C. Sur Deux Produits de l'Agaric Blanc, *Journal de Pharmacie,* 4.11(1870):202–204.

Fleury, G C. Sur l'Influence des Sels de Quinine sur le Développement des Moisissures, *Journal de Pharmacie*. 4.20 (1874):271–273.

Fleury G C. Recherches sur l'Agaric Blanc, *Journal de Pharmacie,* 4.21 (1875a):279–285.

Fleury, G C. Recherches sur l'Inversion du Sucre de Canne par les Acides et les Sels, *Comptes Rendus*, 81(1875c):823–824.

Fleury, G C. Observations sur la Maturation des Dattes. *Journal de Pharmacie,* 4.25 (1877a):417–418.

Fleury, G C. Sur l'Écorce de Goyavier, *Journal de Pharmacie*, 4.28 (1878):188–189.

Fleury, G C. Note sur la Gutta-Percha, *Journal de Pharmacie*. 5.3 (1881):150–151.

Fleury, G C. Sur la Gomme de Grevillea, *Journal de Pharmacie,* 5.9 (1884a):479–480.

Fleury, G C. Remarques sur le Dosage des Alcaloïdes par le Méthode Optique, *Journal de Pharmacie,* 5.20 (1884b):25–26.

Fleury, G C. Sur le Dosage du Tannin, *Journal de Pharmacie,* 6.25 (1892):499–500.

Oudemans, C. Sur le Pouvoir Rotatoire Moléculaire des Alcaloïdes du Quinquina, Isolés ou Combinés aux Acides, *Journal de Pharmacie,* 5.9 (1884):328–348.

Saussure, N. Recherches sur l'Influence du Gas Oxygène sur la Germination de Graines, *Journal de Physique, de Chimie*. 49 (1799):92–97.

Saussure, N. De l'Influence des Fruits Verts sur l'Air Avant leur Maturité, *Mémoire Société de Physique*, 1 (1822):245–248.

Saussure, N. De la Formation du Sucre dans la Germination du Froment, *Journal de Pharmacie,* 19 (1833):587–593.

Saussure, N. Sur la Germination des Graines Oléagineuses, *Bibliothèque Universelle*, 40 (1842):368–371.