

AUGUSTIN-PIERRE DUBRUNFAUT

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ABSTRACT

Augustin-Pierre Dubrunfaut (1797-1881) was a French industrialist and chemist to whom we owe the discovery of mutarotation, d-fructose and maltose, the true nature of invert sugar, the mode of action of diastase and invertase, the application of osmosis to the purification sugar, the large-scale manufacture of ethanol from sugar beets, etc. Dubrunfaut used the Soleil polarimeter to discover the change of the rotatory power of aqueous glucose with time and temperature and to prove that invert sugar was composed of one-half of an equivalent of dextro monorotatory glucose and one-half equivalent of levo liquid sugar (levulose), which could be separated by simple procedures. He demonstrated that lactose also presented the phenomenon of mutarotation. Dubrunfaut analyzed in detail the phenomenon of osmosis, discovered by Dutrochet, and proved that dialysis was a special case of it. This claim brought a bitter discussion with Thomas Graham. He showed that exosmosis could be used to purify sugar very simply. Dubrunfaut claimed that malt diastase was a mixture of compounds, which included the real agent (maltose) altered or modified. Maltose could be economically fabricated in a brewery by precipitation with tannin. He also studied in detail the carbohydrate inulin.

Keywords: ferments; d-fructose; glucose; inulin; maltose; mutarotation; osmosis; starch.

RESUMEN

Augustin-Pierre Dubrunfaut (1797-1881), un químico e industrial francés, al que le debemos el descubrimiento de la mutarotación, la d-fructosa y maltosa, la verdadera naturaleza del azúcar invertido, el modo de acción de la diastasa y la invertasa, la aplicación del osmosis a la purificación de la azúcar, la fabricación en gran escala de etanol a partir de azúcar de betarragas, etc. Dubrunfaut usó el polarímetro de Soleil para descubrir el cambio del poder rotatorio de la solución de glucosa con el tiempo y la temperatura y para probar que el azúcar invertido estaba compuesto de medio equivalente de dextro glucosa mono-rotatoria y medio equivalente de levo azúcar líquido (levulosa), separables por procedimientos simples. Demostró que la lactosa también presentaba el fenómeno de mutarotación. Dubrunfaut analizó en detalle el fenómeno del osmosis descubierto por Dutrochet y argumentó que la diálisis era un caso particular de él, lo que provocó una agria discusión con Thomas Graham. Demostró que la exosmosis podía ser usada para purificar el azúcar en forma sencilla. Dubrunfaut afirmó que la diastasa de la malta era una mezcla de compuestos que incluía el agente real (maltosa) alterado o modificado. La maltosa podía ser fabricada en forma económica en la cervecería por precipitación con tanino. También estudió en detalle el carbohidrato inulina.

Palabras claves: almidón, d-fructosa, fermentos, glucosa, inulina, maltosa, mutarotación, osmosis.

INTRODUCTION

Life and career (Verly, 1869; Glaeser, 1878; Charavay, 1882; Davis, 1930; Fletcher, 1940; Battley, 1998; Anonymous, 2021).

Agustin-Pierre Dubrunfaut was born on September 2, 1797, in Lille (Nord), the son of Adrien François Joseph Dubrunfaut (1763-1820), a liquor merchant, and Marie Anne Michelat. He took his basic education at the Collège de Lille and completed it at the Lycée Napoleon in Pairs, having as teachers the naturalist Pierre Auguste Joseph Drapiez (1778-1856) and the chemist Charles Delezenne (1776-1866), and at the Faculté des Sciences of Paris. Afterwards he returned to Lille and started a brilliant career as an industrialist, particularly in the areas of sugar production and refinery and alcohol distillation. In 1823 he was awarded the Olivier de Serres gold medal by the Société Centrale d'Agriculture for his work on the saccharification of fecula, where he mentioned for the first time the possible existence of the ferment maltose (Dubrunfaut, 1822, 1823). He was a follower of Jean-Baptiste Cellier-Blumenthal (1768–1840), the developer of the continuous distillation column; Dubrunfaut improved the basic design and built columns with diameter of 80 to 100 cm capable of distilling 200 to 4,800 liters of alcohol (92–94 %) per day. He wrote a treatise about distillation, which remained for many years a classical text on the subject (Dubrunfaut, 1824). Educational activities ones accompanied the industrial ones. Between 1825 and 1830 he taught industrial chemistry at the École Spéciale de Commerce de Paris, and at a private school at Bercy (a neighborhood of Paris), dedicated to the teaching of beet manufacture and distillation practice. In 1830 he founded the journal *L'Agriculteur-Manufacturier*, devoted to industry and agriculture, which lasted only three years. In 1867 Dubrunfaut presented his candidature to the position left open at the French Académie des Sciences by the death of François-Olive Rayer (1793-1867). As customary for candidates, he wrote a booklet describing his research activities and achievements (Dubrunfaut, 1868c). He lost the election to Henri-Marie-Bouley (1816-1885) and never tried again. In 1861 he was appointed Chevalier of the Légion d'Honneur and in 1880 promoted to Officier. Dubrunfaut was founder and benefactor of the Société des Amis des Sciences and member of the Sociétés d'Agriculture of Paris, Munich, Bruxelles, Lyon, Lille, Arras, Valenciennes, and Angers, member of the Société d'Encouragement Pour l'Industrie Nationale, etc.

Dubrunfaut passed away on October 7, 1881, at Bercy, by accidental asphyxiation and poisoning by an escape of gas in his room.

Scientific work

Dubrunfaut wrote about 70 papers and books (i.e., Dubrunfaut, 1824, 1825, 1854, 1873) in the areas of analytical, inorganic, and organic chemistry, agriculture, cultivation of beet, manufacture of sugar and alcohol, osmosis etc. In addition to the few subjects discussed below, Dubrunfaut analyzed the fabrication of eau-de-vie and the water most appropriate for its fabrication (Dubrunfaut, 1821); discussed and ordered the different procedures for saccharimetry (Dubrunfaut, 1851a); synthesized and determined the properties of a variety of sucrates (Dubrunfaut, 1851b); determined the heat and mechanical work produced by alcoholic fermentation (Dubrunfaut, 1856e); studied the influence of light upon vegetables and its relation to heat (Dubrunfaut, 1868bd); the phenomena of supersaturation, superfusion, and dissolution (Dubrunfaut, 1869b); catalytic phenomena (Dubrunfaut, 1869c); the nature of ozone (Dubrunfaut, 1870a), the spectra of different compounds (Dubrunfaut, 1870bc), alcoholic fermentation (Dubrunfaut, 1871ab); the combustibility of carbon (Dubrunfaut, 1871c); carbon dioxide as a carburant of carbon in the presence of water (Dubrunfaut, 1872); etc.

His scientific work led to many patents about their industrial application (i.e. (Dubrunfaut, 1829, 1881ab).

Sugar inversion

In 1846 T. Clerget described the use of the Soleil polarimeter for the determination of the amount of crystallizable sugar in different sugar mixtures (Clerget, 1846ab). He wrote that the appreciation of the amount of this kind of sugar depended on its inversion power upon polarized light, when in solutions treated with diluted acids. Jean Baptiste Biot (1774-1862) had already reported that this inversion was constant for every acid and Eilhart Mitscherlich (1794-1863) had recognized that the temperature exerted a temporary influence upon acidified solutions (Biot, 1845, 1846). According to Clerget, the value of the inversion coefficient (the ratio between the deviation of the plane of polarized light after acidification and the primitive deviation) of HCl was 38/100 at 13 °C and 29/100 at 30 °C and between 10° and 30 °C varied linearly with the temperature (Clerget, 1846a). Clerget described in detail the procedure for determining the value of the coefficient and its use in the analysis of sugar matter at any temperature (Clerget, 1846b).

In 1846 Dubrunfaut reported that he had obtained a Soleil polarimeter and repeated Mitscherlich's experiment on the effect of temperature on the rotatory power of inverted sugar (Dubrunfaut, 1846). He had put warm syrup in a tube filled with nitrous gas and measured the sense and intensity of the alteration of the rotatory power with the decrease in temperature. He observed that the rotation sense changed from left to right at temperatures below 100 °C. This substantial change caused by heat, suggested its use for the direct measurement

of the proportion of "liquid sugar" mixed accidentally or purposely with commercial crystallizable sugar [The name liquid sugar was changed to *levulose* by Marcelin Berthelot (1827-1907) and to *d-fructose* by William Allen Miller (1817-1870) (Miller, 1857)].

The solution of this problem required the previous determination of the constancy of the rotatory power of liquid sugar at a given temperature, its variation with temperature, the exact determination of this sugar present in commercial sugar in relation with the rotatory power of sugar cane, and the possible transformation of the latter by temperature. Availability of this information, together with the measurement of the displacement of the plane of polarization at two very different temperatures, allowed determining the relative amounts of cane sugar and liquid sugar present in a given mixture (Dubrunfaut, 1846).

Dubrunfaut wrote that Clerget's paper had appeared shortly after he had begun his experiments and this fact had forced him to publish his results in an incomplete form, containing, for the moment being, the examination of the solutions of cane sugar, fruit sugar, glucose, dextrin, and rock crystal perpendicular at the axis. He mentioned that Clerget had operated upon warm acid syrup; under this condition it was impossible to make an accurate measurement because the inversion ratio varied not only with the different acids, but it also did with the proportion of a given acid, *and* with the temperature. For example, acid syrup having a ratio of 10° at 35 °C would not return the same value when cooled to 10 °C (Dubrunfaut, 1846).

Dubrunfaut went on to describe the experimental procedure, the temperature corrections applied, and results obtained when using (1) syrup of inverted sugar; (2) cane sugar; (3) beer yeast; (4) a solution of glucose; (5) hydrated glucose; (6) and dextrin. For example, the rotatory power of a warm solution of glucose did not vary sensibly between 18° and 80 °C. The immobility of the plane of polarization was only apparent because taking into account the correction for the thermal expansion of the tube and the syrup it was found that for a variation of 100 °C, in the range 0° to 100 °C, the value of the rotatory power at 0 °C had moved by 0.0462 to the right. Pure glucose was found to have the same rotatory power, independent of its origin. This result was found to be true for grape sugar, glucose prepared in the laboratory from starch, and glucose from honey (Dubrunfaut, 1846). Hydrated glucose had a fresh taste, a phenomenon that could be explained by the fact that the dissolution of glucose in water was an endothermic process: 20 g of sugar dissolved in 100 cm³ of water experimented a temperature decrease of 4 °C. The corresponding decrease with sugar cane was only 0.5 °C. This result implied that the transformation of crystalline inverted sugar into glucose was accompanied by a decrease in temperature and that the crystallization of sugar should be also accompanied by a decrease in temperature, if conducted instantly (Dubrunfaut, 1846).

Dubrunfaut found that dissolving glucose of formula C₁₂H₂₈O₁₄ in pure hot alcohol, followed by precipitation, produced glucose of formula C₁₂H₂₄O₁₂ (Dubrunfaut, 1846). The truth of this transformation was easily demonstrated without analytical analysis by the elevation of the rotatory power of both sugars that was in inverse ratio to their molecular masses. This power was essentially present in C₁₂H₂₄O₁₂ and was independent of the molecules of crystallization water. The latter sugar could be heated to 100 °C without aqueous fusion. Rapid solution in water of the sugar C₁₂H₂₈O₁₄ in a tube at 12° to 15 °C showed that it had a rotatory power double the value reported by Biot. Heating the tube was accompanied by a change of the rotatory power towards the value 0, which differed little from that of dissolved glucose and from the value assigned by Biot. This change occurred also place at room temperature, although it took a longer time. This property was common to glucose of all origins. This retrograde rotation (*mutarotation*) of the glucose dissolved was very sensitive during the first moments of the experiment. Thus, it was impossible to maintain the absolute numerical value of the effect because it was not known what happened during the time of dissolution, which itself was accompanied by a decrease in temperature (Dubrunfaut, 1846).

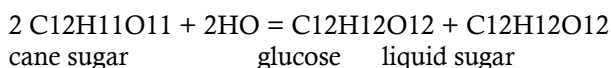
According to Dubrunfaut, scientists had not accepted the composition of invert sugar he had proposed (Dubrunfaut, 1847b, 1849). He now presented additional experimental information to justify his claim (Dubrunfaut, 1856d). He wrote that he had used cane sugar chemically pure that had lost only 0.001 of its weight by drying at 100 °C; repeated burning had indicated that it contained, by weight, 42.2% of carbon, corresponding to the formula C₁₂H₁₁O₁₁. Its molecular rotatory power was (α)_j = +73.84, slightly higher than the value +72 reported by Biot. The difference was probably due to the higher degree of purity of the sugar he had employed. Inversion of this sugar by means of acid produced an inversion coefficient of 0.380, the same as reported by Biot. This coefficient varied continuously with temperature in all the possible temperature range. It was -28.059 at 14 °C, -14.0295 at 52 °C, and 0 at 90 °C. Invert sugar, dried at 100 °C under vacuum, experimented an increase in weight of 0.05 above that of the primitive cane sugar, justifying the conversion of non-fermentable cane sugar to fermentable sugar:



This meant that the rotatory power of invert sugar at 14 °C, reported in relation to sugar of formula C₁₂H₁₂O₁₂, was -26.652 and -24.224 in relation to the dihydrate C₁₂H₁₂O₁₂·2H₂O (Dubrunfaut, 1856d).

Dubrunfaut added that solidification of a concentrated syrup of invert sugar separated dextrorotatory glucose that lost 0.095 of its weight, after purification and drying at 100 °C. Chemical analysis indicated that it contained, by weight, 39.8% carbon, corresponding to the formula C₁₂H₁₂O₁₂. Dissolved in water it presented the expected two rotatory powers, identical to those of grape sugar and diabetes glucose. Dubrunfaut reported the values (α)_j = +53.2 for the compound C₁₂H₁₂O₁₂ and (α)_j = +48 for C₁₂H₁₂O₁₄. He also mentioned that treating an aqueous solution of invert sugar with limewater resulted first in the formation of a very fluid milky emulsion that solidified into a very consistent mass. Pressing this mass between pieces of cloth separated a liquid that contained all the dextro glucose as soluble calcium glucosate. The insoluble part contained a crystallized basic calcium succinate from which oxalic acid allowed separating liquid sugar in a very pure state. Drying this non-crystallizable sugar under vacuum turned it into a sugar having the same constitution as invert sugar and glucose, represented by the formula C₁₂H₁₂O₁₂ and having rotatory power (α)_j = -106 at 14 °C. Dubrunfaut repeated his claim that invert sugar was composed of one-half of an equivalent of dextro monorotatory glucose and one-half of an equivalent of levo liquid sugar. Addition of the rotatory power of these amounts, $106/2 - 53/2 = -26.4$, yielded almost exactly the rotatory power of inverted sugar, (α)_j = -26.652 (Dubrunfaut, 1856d).

A series of additional experiments confirmed the fact that it was possible to use simple procedures to separate from invert sugar, without alteration, two sugars having different chemical properties and antagonistic rotations. In other words, the following relation could represent the constitution of invert sugar (Dubrunfaut, 1856d):



A following paper described in detail the procedure for separating dextrorotatory glucose from levorotatory glucose (levulose) by means of limewater (Dubrunfaut, 1869d). The resulting calcium levulosate was decomposed with CO₂ into a sugar solution having rotatory power of 44 to 45° at 14 °C and 33 to 34° at 52 °C. The purified levulosate appeared as small prismatic needles having double refraction, sparingly soluble in pure water, and decomposable by warm water at 40° to 50 °C. Dubrunfaut mentioned that his method was particularly applicable to the analysis of sweet fruits and all products containing invert sugar, such as honey, sugar molasses, etc. The enormous importance of invert sugar as food meant a strong interest in industrial analytical procedures. Dubrunfaut experiments proved that levulose had a sweetening effect equal to that of cane sugar and larger than that of dextro glucose. Hence, the significant economic impact of a process able to separate grape sugar and fruit sugar into a fraction that replaced cane sugar by sweet syrup and the starch glucose used for industrial purposes (Dubrunfaut, 1869d).

Fermentation

In 1843 Mitscherlich reported that the fermentation of grape sugar (glucose) and liquid sugar yielded alcohol directly, without passing through an intermediate state and maintaining the direction of their rotatory power (right for the first, left for the second). This result indicated that the sugars themselves were the site of the fermentation (Mitscherlich, 1843). Biot had observed a similar result for the liquid sugar of fruits, but he believed that cane sugar transformed first into fructose and then into alcohol. Eugène Souberain (1797-1859) studied this phenomenon in detail and concluded: (1) fermentation changed cane sugar not into glucose but into liquid sugar having a levorotatory power; (2) cane sugar did not transform immediately and completely into fructose; it did it by a very slow process; and (3) fermentation transformed glucose into liquid sugar without going through an intermediate state (Souberain, 1843).

According to Dubrunfaut, Mitscherlich and Souberain were wrong in assuming that inverted sugar kept its levorotatory power during the whole fermentation process (Dubrunfaut, 1847b). In fact, Dubrunfaut measurements of the rotatory power (reduced to 13 °C) during the fermentation of a solution of inverted sugar, indicated that this property did not change as long as about 3/5 of the sugar had not yet been converted into alcohol. Following the reaction with a polarimeter showed that beyond this percentage the amount of alcohol produced grew in arithmetic progression while the degree of deviation disappeared in geometrical progression. This simple optical procedure was enough to prove that this type of sugar was not a simple substance; it was composed of heterogeneous elements having *opposite rotations*. To avoid circumlocution, Dubrunfaut suggested naming this type of process *elective alcoholic fermentation* (Dubrunfaut, 1847b).

Dubrunfaut conducted many similar experiments with artificial mixtures of sugars, with known mixtures of pure crystalline glucose and inverted sugar, with inverted sugar subjected to a fermentation, etc. and concluded

as follows: (1) inverted sugar and its similar varieties (grape sugar, fruit sugar, etc.) were not sugars *chemically simple*. They did not transform into glucose by crystallization, as reported by some; this phenomenon could only eliminate a certain proportion of well-characterized glucose, while the levorotation of the mother water was increased by any deflection power of opposite sign carried by the glucose; (2) it was possible to use various processes to separate from the inverted sugar a non-crystallizable sugar having, among other characteristic properties, a levorotatory power, which, at 14 °C, was three times that possessed by the inverted sugar at the same temperature. This sugar did not seem to have been brought to a degree of purity that could be considered as simple; (3) the alcoholic fermentation of the invert sugar, studied with a distillation still and optical chemistry devices, showed that this sugar was not simple. In fact, the sugar which disappeared first was optically neutral while that which disappeared last was the non-crystallizable and strongly levorotatory sugar mentioned previously; (4) lactic fermentation also produced a kind of analysis in invert sugar; only its initial action, instead of focusing on a neutral compound, as alcoholic fermentation did, occurred on glucose, which appeared to pre-exist already formed in invert sugar; and (5) alcoholic fermentation, applied to simple mixtures of sugars, did not appear to produce analytical reactions. The transformations that took place on simple sugar mixtures were the same as on separated sugars without choice or preference. The quantities of the two sugars which decomposed at all the periods of the fermentation, remained in the same ratio as that of the original mixture (Dubrunfaut, 1847b).

In a following paper Dubrunfaut repeated his previous claim that Mitscherlich and Souberain were wrong in claiming that invert sugar and fruits sugar were bodies chemically simple (Dubrunfaut, 1849). He had also shown that honey sugar differed from fruit sugar in containing cane sugar, characterized by the inverse action of the ferment upon it, and that the fermentation of honey molasses was characterized by an inversion to the right, a fact that seemed to indicate the presence of a new sugar. Invert sugar was probably composed of two sugars having opposite rotation; one of these was crystallizable glucose and the other non-crystallizable levorotatory sugar (today, *D-fructose*). In this new paper Dubrunfaut presented the results of many experiments that proved correct his assumption (Dubrunfaut, 1849). These results were divided in three groups:

(1) Invert sugar and similar sugars

Cane sugar, well inverted by weak acids or by ferments, is basically composed of one equivalent each of two different sugars, mixed or combined. One of them is crystallized glucose, which in the anhydrous state has the formula $C_{12}H_{22}O_{11}$; the other is non-crystallizable sugar, which dried at 100 °C has the same composition and formula of glucose, and upon fermentation yields the same amounts of alcohol and CO_2 than glucose. The new sugar is levorotatory with a rotatory power four times larger than that of invert sugar at the same temperature and conditions. This rotation increases by 9/37 when heated from 14 °C to 52 °C. It combines with lime forming a basic and soluble substance similar to the one formed by glucose. It is unstable in contact with air, yielding new compounds yet to be examined. With lime it also forms sparingly soluble compounds crystallizing as microscopic prismatic needles, unstable in water, air, and heat. Sugar cane, heated alone or in the presence of water or weak acids, yields a liquid sugar identical to the one prepared from inulin (Dubrunfaut, 1849).

(2) Honey. Commercial honey contains variable amounts of cane sugar, present only in the liquid fraction. This sugar disappears with time due particularly to inversion produced by the natural ferment it contains. The characteristic flavor of honey is a result of the elements generated by an alcoholic fermentation. Honey, under pressure, produces about 20 to 30% of glucose, the remaining mother liquor is strongly levorotatory. Honey, left alone in ill closed vessels located in caves, go through a slow fermentation under the influence of a natural ferment. This ferment acts initially over the liquid sugar leaving a molasses concentrated in glucose. Honey contains, without exception, a large proportion of fruit sugar, from which the new sugar can be easily separated by means of lime. Honey contains, in addition to cane sugar and the elements of fruit sugar, an excess of glucose or another dextrorotatory sugar (Dubrunfaut, 1849).

(3) Dry or skimmed grapes. Commercial raisins have dextrorotatory syrup; under the influence of foreign agents, they experiment with time alterations that attack first the liquid sure. These alterations are the result of a natural fermentation analogous to the one experimented by honey, and by the attack of diverse insects, mainly *Acarus farinae*, acting on the liquid sugar (Dubrunfaut, 1849).

Milk sugar (lactose)

Dubrunfaut repeated his finding that an aqueous solution of glucose had the property of offering two different rotatory powers at the same temperature, the largest one at the moment that the solution became cold and the other, several hours later. The ratio of the two values, 66/35 did not include the effect that took time during the dissolution process itself. Eventually he was able to find the law that described the sudden change of the rotation with time and to determine that the rotatory power of the mameionated glucose was double that of the glucose modified by the dissolution. Dubrunfaut distinguished the two states of glucose by the names *monorotatory* and *birotatory* (mutarotation). This phenomenon was unusual, it represented an example of the

profound modification of the physical and chemical properties that a given substance could experiment under *indifferent* conditions. Dubrunfaut added that his experiments with lactose had provided the necessary proof of this fact (Dubrunfaut, 1847a, 1856a).

It turned out that the same as glucose, the optical rotation of milk sugar was much larger at the time of its dissolution than afterwards. The intensity of the change in rotation varied with the temperature, it was very slow at 0 °C and instantaneous at 100 °C. This result led Dubrunfaut to study in detail the properties of lactose. Lactose purified by repeated crystallization, dissolved in water with release of heat and was three times more soluble in water than crystalline sugar. It was little hygroscopic, heated to 150 °C in dry air it lost 0.05% of its weight without showing alteration. Chemical analysis indicated that it contained, by weight, 39.70% carbon and 60.07% water, corresponding to the formula $C_{12}H_{12}O_{12}$ (dried at 100 °C).

Its lime sucrate contained one equivalent of base. Heated to 100 °C in the presence of sulfuric acid increased its rotatory power and transformed it into a substance partially putrescible, which Dubrunfaut was unable to mamemlonize or crystallize. Treated with nitric acid converted it into mucic acid. The initial effect was an increase of 13/10 in the rotatory power to the right followed by a decrease towards 0 and another increase to about 1/4 of the primitive value of the milk. With beer yeast it yielded a large amount of CO₂ and no alcohol, without changing the rotation (Dubrunfaut, 1856a).

In 1856 Antoine Béchamp (1816-1908) tried to explain the phenomenon of mutarotation in glucose by assuming that the glucose modification infusible at 100 °C, in contact with water, momentarily reconstituted the hydrate $C_{12}H_{12}O_{12} \cdot 2H_2O$ (having the highest rotatory power) to pass imperceptibly to the fusible modification of glucose, $C_{12}H_{12}O_{12}$ (having the weakest rotatory power). This result, independently of the variation of the rotation, proved that the fusible glucose absorbed humidity to become syrupy while the second modification remained dry (Béchamp, 1856a). This explanation led Dubrunfaut to repeat his experiments in order to verify his conclusions (Dubrunfaut, 1856b).

He found that drying carefully the glucose hydrate to eliminate the two equivalents of water without disturbing its crystalline constitution, did not affect its two rotatory powers, which remained in the ratio 2:1 he had assigned to pure glucose (Dubrunfaut, 1856a). If true, these results meant that the water of hydration did not influence the variable rotation of the sugar. In addition, drying the glucose with fusion and dissolving it in water produced the facts reported by Béchamp. Thus, independently if the fusion was made with or without loss of the hydration water, the rotation of the dissolved glucose stayed unchanged and gave immediately the lowest rotatory power. These results suggested that both rotations originated from profound molecular modifications produced successively and alternatively by the crystallization and by dissolution or fusion. This explanation was similar to that applied to lactose and the glucosolate of common salt. Perhaps this variable rotation was only a manifestation of particular situations in the phenomena of crystallization and dissolution. For example, Dubrunfaut had already demonstrated that dissolved lactose was clearly different from crystalline lactose not only by its rotatory power but also by a lower solubility. Mamelonated glucose also presented two different solubilities in water (Dubrunfaut, 1856b).

Osmosis

Dubrunfaut wrote that in 1820 Mathieu de Dombasle (1777-1843) had observed that sliced raw beets were inert to maceration but did it strongly when previously dried or heated to 100 °C (Dombasle was one of the first French agronomists to grow beetroot to produce sugar). Dombasle assumed that the desiccation or cooking had induced in the vegetable tissue a modification, which assimilated it to inert chemical substances allowing it to obey only the laws of affinity and cohesion. Dombasle named this modification *depreciation* (amortization). In other words, Dombasle assumed that maceration or osmosis did not take place on dead cells (Dombasle, 1820; Dubrunfaut, 1855, 1873). Posterior work by Henri Dutrochet (1776-1847) (Footnote 2) proved clearly that this assumption was wrong, osmosis applied very well to the living cells (Dutrochet, 1826). Dutrochet discovered that two liquids, separated by an organic membrane, gave place to two streams, mostly dissimilar, that penetrated and transversed the pores of the membrane. The strongest stream moved almost all the time, from the less dense liquid to the denser one with such vitality that it overcame all obstacles opposing its movement. Dutrochet named this effect *endosmosis*. His experimental apparatus (endosmometer) and procedure were very simple: A vase closed at his bottom by a membrane was filled with a dense liquid and then introduced into another vase containing a less dense liquid. Under these conditions the strong stream traveled from the internal to the external vase (endosmosis), and the weaker one in the opposite direction (exosmosis). This led him to consider the existence of a new force (to the exclusion of the vital force of the vitalists) able to explain many organic functions, in particular, the source and cause of the vital movement in vegetable and animals. Nevertheless, all the experiments made by Dutrochet with his endosmometer proved that he did not negate the osmotic force to the dead cells. The fact observed by Dombasle was correct, slices of unamortized beet did not undergo maceration, while did when they had been depreciated (Dutrochet, 1826; Dubrunfaut, 1855, 1873).

In a first paper on the subject, Dubrunfaut explained the apparent contradiction between the findings of Dombasle and those of Dutrochet, as follows: (1) beet pulp resisted maceration, this resistance increased as the size of the slices decreased; (2) the amortization procedures recommended by Dombasle produced in the tissue a strong disaggregation; (3) the opaline aspect of the beet slices was due to gas contained in the intercellular lacuna; this gas, the same as the normal adherence of the cells, impaired the penetration of the macerating liquid into the cells and antagonized the double current of the osmotic force; (4) the osmotic force would nevertheless eventually overcome without amortization these resistances, as long as secondary reactions did not disturb the useful result of the maceration by more or less profound and varied alterations, like the mucus and lactic fermentations; and (5) finally, the cell in the fresh and undamped beet was in a state of turgescence that made it unsuitable for endosmosis (Dubrunfaut, 1855, 1873).

Dubrunfaut believed that acids would probably amortize the beet slices. This assumption was justified experimentally; diluted acids produced this reaction, in particular, sulfuric acid employed in the dose of 4 to 5/000 the weight of the roots produced it already at 15 °C, without affecting in the minimum the crystallizable sugar, contrary to the scientific prediction; solutions of sugar under these conditions were strongly affected. Acid salts, alkalis, alkaline salts, and acid wines produced the same effect. Dubrunfaut used this result to develop an industrial distillation process of beets based on triggering them to ferment while in slices, with acid water or beet wine containing the pertinent ferment. This fermentation protected the roots from all alteration and resulted in the replacement of the cellular sugar by its equivalent amount of alcohol, which could be eliminated by maceration of distillation (Dubrunfaut, 1855, 1873).

Dubrunfaut thought about the possibility of using exosmosis to purify sugar. Previous work had shown him that raw beet sugar contained substantial amounts of glucose or the similar impurities detectable by means of the Fehling liquor. All the refined sugar sold in Paris contained non-crystallizable sugar and had an acid reaction. The proportion of glucose varied between 3 to 10/000, a considerable amount for a white grained sugar, previously considered pure (Dubrunfaut, 1855, 1869a, 1873). In this paper he presented the first version of the process, directed to the purification of beetroot molasses and the extraction of their sugar. This molasses were a mixture of sugar and organic and inorganic salts, particularly potassium nitrate and chloride. Placing this molasses in contact with water in a Dutrochet endosmometer established two streams, where the stronger moved from the water to the molasses while the weaker did in the opposite sense. The latter stream, an aqueous solution of the organic and inorganic salts, left in the endosmometer a sugar diluted with the coloring matter and a small fraction of the salts. This molasses had lost its bad flavor and was edible like cane molasses. Subject to the usual operations it yielded crystallizable sugar. The water loaded with salt was then concentrated and precipitated the dissolved salts (Dubrunfaut, 1855, 1873).

In a later publication, Dubrunfaut wrote that the above procedure contained all the elements of a general analytical procedure, applicable in the laboratory and industrially. In the manner of dialysis, it used the Dutrochet endosmometer as the dialyzer (Dubrunfaut, 1866ab). The results of the practical application of Dubrunfaut procedure were presented by Camichel of Camichel et C^e, at Saint-Claire de la Tour-du-Pin, at the 1867 Exposition Internationale (Paris) and won a medal. A bitter discussion about priority of the discovery took place between Dubrunfaut and Thomas Graham (1805-1869). The interested reader will find the details in Dubrunfaut's book about osmosis (Dubrunfaut, 1867, 1868c, 1873, pp xvii-xxvii).

Maltose

Dubrunfaut wrote that nothing was known about the active ingredient of malt (*maltine*), its mode of action, or the conditions most favorable for its action. Diastase had been signaled as the active component, but this substance was only a mixture of compounds, which included the real agent, altered or modified (Dubrunfaut, 1868af, 1879). He now wanted to justify these contentions and provide what he thought were the most rational and economical conditions for its use. The active component of malt, of which he had indicated its existence in 1822 (Dubrunfaut, 1822, 1823), was soluble in water, was albuminoidal or glutinous, and contained a high percentage of nitrogen. The malt infusion, prepared at a temperature below 40 °C, did not affect it and the infusion itself also acted upon the fecula with the same intensity as the malt. In the high dose employed in industry (20 to 25% of the weight of the starch) the liquefaction and saccharification occurred rapidly. Heating at 70° for two hours an infusion of known power precipitated a substance that after washing was completely inactive and contained about 15% of nitrogen, a level corresponding to an albuminoidal substance. Treating a malt infusion of known strength with concentrated alcohol until refusal of precipitate, resulted in the precipitation of crude diastase; it was easy to realize that the precipitate did not represent all the power of the active infusion and that the missing fraction was not present in the alcoholic solution. These facts indicated that the alcoholic treatment recommended for the preparation of the raw diastase partially spoiled the properties of the active substance as it existed in the malt. Dissolution in water of the raw diastase precipitate left an insoluble matter, which contained only 8 to 9% of nitrogen, proving that alcohol had altered the active component.

Dubrunfaut added that treating the infusion with 2 or 3 times its volume of concentrated alcohol was enough to eliminate all the active component as flakes, easy separable. Treating the infusion with a solution of an astringent component, such as tannin, gallnut, or sumac, produced a flaky precipitate, insoluble in cold water, composed by a combination of the tannin or tannic acid with the active component of malt. It seemed that in this compound the active component played the role of a base. The residue of the infusion was depleted of the active component, as shown by its inactivity over starch paste (Dubrunfaut, 1868af, 1879).

According to Dubrunfaut his results proved that (1) maltine possessed all the active properties present in the malt or in its infusion, prepared at low temperature; (2) all the procedures for isolating the active component altered it significantly; (3) all the procedures for isolating diastase provided a mixture of several ill-defined products (dextrin, carbohydrates, etc.) mixed with the modified active matter; (4) malt contained at least 0.01% of maltine, enough to liquefy 100 to 200,000 times its weight of faculae, showing its tremendous strength compared to diastase; (5) the active matter contained a large percentage of nitrogen, was albuminoidal and levorotatory, and heat labile; (6) maltine was precipitated by concentrated alcohol and tannin; and finally (7) maltine could be manufactured economically in a brewery by treating cold malt, or malt at 30 °C, with 4 to 5 times its weight of water. The liquid should then be treated with tannin or sumac infusion and the resulting precipitate separated and pressed to eliminate the attached liquid (Dubrunfaut, 1868af, 1879).

Glucose

Dubrunfaut wrote that Dumas had given the name *glucose* to diverse sugar products that presented a confuse crystallization and that could be isolated from fruits, diabetes urine, honey sugar, etc. ("la sucre de raisin solide a été assimilé au sucre dans lequel l'amidon se convertit sous diverses influences, il l'a été également au sucre de diabète, au sucre de miel, et, en général, on a été disposé à confondre en une seule espèce les sucres solides qui se présentent en masses cristallines, sans formes déterminables") (solid grape sugar that had been assimilated to sugar in which starch converted under various influences; it had also been assimilated to sugar of diabetes, to sugar of honey, and, in general, it had been disposed to be confused in one alone species solid sugars that occur in crystalline masses, without determinable forms" (Thénard *et al.*, 1838).

Dubrunfaut added that the glucose he had separated from the reaction of malt over starch had also been considered to be identical to the above-mentioned glucoses, until the polarimeter observations of Biot had shown that malt glucose possessed a rotatory power substantially larger than the other glucoses (Dubrunfaut, 1847b). He now reported some new properties of this glucose and compared them to those prepared from grapes. The substance seemed to crystallize in rhombohedral forms, like grape glucose, but had a rotatory power three times larger than the latter. It did not present the elective fermentation discussed before but boiled for a long time with sulfuric acid it became identical with grape glucose. It was the initial fermentable product of the reaction of acid over starch and the final of the reaction of nitrogenous matter over the same substance (Dubrunfaut, 1847b).

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Inulin

In 1804 Valentin Rose (1762-1807) reported the discovery of a new carbohydrate (inulin) in the root of elecampane (*Inula helenium*) (Rose, 1804). He found that a concentrated decoction of the root, after standing for several hours, deposited a white powder that appeared at first sight much like starch but differing in its

principles and properties. Inulin was insoluble in cold water and well soluble in boiling water. A solution of one part of inulin with one part of alcohol was at first clear and then precipitated a swollen white sediment, leaving a clear fluid. Nitric acid transformed inulin into malic and oxalic acid. According to Rose, inulin was a material intermediate between gum and starch (Rose, 1804).

Dubrunfaut wrote that various scientists had studied the properties of inulin and reported conflicting results; this led him to investigate it further (Dubrunfaut, 1856c). He found that independent of the origin of inulin, it always presented the same physical and chemical properties but prepared according to the dry process it appeared as translucent as gum, or opaque like starch. Dried at 100 °C it lost 16% of its weight, not additional losses occurred up to 180 °C. Afterwards it yellowed and melted at 190 °C with decomposition and loss of weight. Chemical analysis of inulin dried at 100 °C indicated that it contained, by weight, 44.321% carbon and 55.679% water, corresponding to the formula $C_{12}H_{10}O_{10}$ (today we know that inulin is a polymer of formula $C_{6n}H_{10n+2}O_{5n+1}$). Dried inulin absorbed water rapidly; transparent inulin, put in water, turned opaque, swelled and became hydrated. It did not ferment in contact with yeast beer or diluted acid in water or in a solution of tartaric acid.

Dubrunfaut mentioned that inulin was present in large proportion in many products used as foodstuff by humans; it could be extracted from them and used commercially like starch and fecula (Dubrunfaut, 1856c)

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