The Synthesis of Cane Sugar.

THE END OF A CHAPTER.

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THE synthesis of cane sugar in the laboratory has brought to triumphant completion a long chapter of endeavour on the part of the chemist. It has always been regarded as the crowning success to be won in the long series of victories achieved by the chemist in synthesising natural organic products, which began with Wöhler's first synthesis of urea a hundred years ago. It is of considerable interest, therefore, to indicate some of the stages of progress and the lessons which have been learned from them. A technical and, even more, a commercial synthesis of this product of the sugar cane and of the beet remains to be effected, but the possibility of doing this in competition with the plant is very remote.

The origin of the sugar cane is obscure, but it is known that it has been cultivated in eastern tropical Asia from great antiquity and that it spread westwards and eastwards, reaching the new world early in the sixteenth century, and the West Indies in 1641. Markgraf in 1747 was the first to find sugar in the beet, thereby pointing the way to the foundation of the beet sugar industry in Europe, which did not actually commence, however, until 1801.

Naturally, cane sugar early engaged the attention of the chemist, and the first experiments to determine its empirical formula date from Lavoisier, though it was only definitely established by Liebig in 1831. Whilst the question of the constitutional formula of the sugars, and of cane sugar in particular, has persistently occupied the activities of many chemists, the chief progress made will always be associated with the name of the master, Emil Fischer, whose achievement in unravelling the complex stereochemical relationships of the isomeric hexose sugars and in effecting their synthesis stands second to none other in the domain of organic chemistry.

Sucrose was shown to be a compound of the two simple hexose sugars, glucose and fructose, combined together in such a manner that the product was highly susceptible to hydrolysis by the weakest acids, but very stable towards action by alkalis. As the investigation continued it became clear, partly owing to the work of Tollens, that glucose and fructose, when in combination with other substances, existed preferentially, if not entirely, not as aldehyde and ketone respectively, but behaved as if they had the structure of compounds containing a carbon-oxygen ring. For a long time this ring was considered to consist of four carbons and oxygen, though it is true that the assumption was based mainly on the analogy with the acid lactones and was without any definite chemical evidence. The hypothesis gave a ready explanation of the existence of two isomeric series of glucose derivatives and of isomeric glucosides.

The constitutional formula of cane sugar was formulated by Fischer and by Tollens on the basis of a four carbon-oxygen ring structure for its components, and many attempts were made to effect its synthesis by combining them or their derivatives in synthesising natural products. In no case were these efforts—and they were numerous in the years 1890 to 1910—rewarded by success. A claim by Marchlewski in 1891 has never been accepted by sugar chemists, and even the possession of crystalline acetochloro derivatives of the sugars failed to give the much-sought-after cane sugar.

The work of the St. Andrews school, started by Purdie, particularly of Irvine, in studying the methylated derivatives of the carbohydrates opened up a new field of investigation, out of which it was found that glucose reacted in other forms than the accepted stable ring, and afterwards that the supposed ring structure of glucose itself had to be challenged. The work during the next decade, after some disillusions, has evidenced further complexity in this already complicated field. Suffice it to say that it has been proved for each of the sugars that it can react in more than one ring form according to circumstances, whilst the particular ring form present in reference compounds has been studied. In this connexion the work of Haworth deserves the highest possible recognition.

There was thus established an up-to-date formula for sucrose—differing very little, it is true, from that of Fischer and Tollens—which enabled once more hopes to be held out of effecting the so long sought synthesis. Hopes, but no certainty, for, as workers in the field of the sugars know well, the experimental difficulties are extreme, because, whilst the glucose element in sucrose is, in the stable so-called α-modification, easy to make and to purify in the form of its compounds, the fructose element is, in the γ-modification, which is unstable, difficult of isolation, even in its derivatives, and likely to change. The many efforts of a thoroughly systematic and scientific character to effect the synthesis of sucrose from the requisite derivatives of α-glucose and γ-fructose have met with no better success at the hands of Irvine and his school, of Haworth and his co-workers, than attended those of Fischer and Armstrong, Ryan and others, all of whom had the potential components of the elusive sucrose at their disposal. Complex mixtures, apparent isomerides of sucrose itself, always resulted.

More success has now attended the efforts of our Swiss colleagues, Pictet and Vogel, who, working on much the same lines as their predecessors, sought to condense the tetra-acetate of α-glucose with the tetra-acetate of γ-fructose in the presence of phosphoric anhydride. A complex mixture resulted, from which a well-marked crystalline constituent was separated on solution in boiling alcohol and subsequent cooling. This product has proved to be identical with sucrose octacetate in melting-point and optical rotatory power.

On hydrolysis, cautiously effected by means of sodium methylate, sucrose itself was obtained in measurable crystals. Naturally, in a matter of such importance, the identification of the synthetic sugar has to be very complete. Pictet and Vogel's product had the correct optical rotatory power both before and after inversion ; the melting-points of the modifications, crystallised from ethyl alcohol and from methyl alcohol, were also the same as those of the natural product : sweetness and other properties were in accordance with expectation. There seems no room for any other course than a whole-hearted acceptance of the synthesis and the congratulation of Pictet and Vogel on their truly great achievement.

Much is to be learned from this chapter of chemical science—not the least being the value and necessity of manipulative skill of the highest order, *involving* an apprenticeship and a practical training of a rigour which is sometimes in danger of being overlooked to-day. Again, there can be no better example of the need of maintaining an open critical mind towards accepted conclusions and the advantage of reopening a question, in spite of apparent finality, when new view-points arise.

Writers of detective fiction have taught us that the end of a chapter is by no means the least exciting portion, and this is obviously true of the sucrose chapter. If its structure has now been established and confirmed by synthesis, more than ever is it necessary for the organic chemist to look inside the molecule so as to explain, for example, its behaviour on acid hydrolysis and the readiness with which the hexose molecule can assume different forms. The original formula of glucose, as an aldehyde, postulated a very active substance ; perhaps we shall learn how and why this may react in many different modifications according to circumstances, thus providing a clue to reactions in the plant and in the animal.

The physicists proceed apace with a knowledge of the structure of the atom ; in the domain of contact catalysis, much has been done to gain an explanation of the nature of absorption at the surface of a catalyst, and an understanding is being sought of how a catalyst works,—whether, for example, an impact of energy proceeds from one point in an organic molecule, at which it is received, along a carbon chain to another point at which the actual chemical change occurs.

It may well be that the study of the subtle changes in internal structure in the sugar group, where a unique series of highly specific catalysts is available, will be highly fruitful, and it is with this hope that we confidently await the beginning of the new chapter. The one we close is full of fame—a long list of honoured men of science of all nations, of which but a few have been mentioned, have each in their turn contributed to a problem which has all too long baffled solution. There can be no more appropriate celebration of the centenary of the first organic synthesis.

The Artificial Silk Industry.

AMONG the new industries of the present century, there are few which have developed so rapidly as the artificial silk industry. In a " Survey of Textile Industries "[1] recently issued, much interesting information is given about this now important industry. It is pointed out that scientific research and experiment have played an essential part in its development. Production on a commercial scale dates back to 1896, when a few hundred tons were produced in France by the nitro-cellulose or ' Chardonnet' process, though since then the viscose, acetate, and cuprammonium processes have been perfected. Of these, the viscose is now the most general, and is estimated to account for at least 80 per cent of world production. Each of the methods differs to some extent in regard to the raw materials used, and also in the chemical treatment employed. Their respective products vary from each other in regard to strength, fineness, lustre, permeability to moisture, etc. In all, however, the essential feature of their manufacture consists of a succession of chemical processes applied to cellulose, derived generally from wood or cotton. In the viscose method, for example, sulphite wood pulp, obtained from pine or spruce logs, forms the raw material. The cellulose is first converted into a viscous pulp, which is then squeezed through small nozzles and emerges in the form of continuous filaments, which after further chemical treatment can be converted into yarn by a ' doubling process.' More recently, it has been found possible to produce short lengths known as ' staple-fibre,' which can be spun like cotton or wool.

In the Committee's report it is shown that, from a commercial point of view, artificial silk has certain important advantages over cotton, wool, or natural silk. Its price is not affected by fluctuations in supply due to unfavourable weather or the ravages of insect pests. Its raw material (timber) is abundant, and output can be expanded (with the proviso that steps may have to be taken eventually to safeguard future timber supplies) to almost any extent by the erection of the necessary factories. Its price is mainly dependent on the cost of manufacturing processes, and these are more amenable to human control than are the direct products of Nature. Nor is its production necessarily confined to nations possessing a particular type of climate or other natural resources. The industry has, in fact, been developed mainly in industrial countries which, besides being favourably situated for obtaining raw material, possess a well-developed chemical industry and a supply of trained chemists and other skilled employees.

As is well known, there has been a remarkable expansion of the industry since the War. At first, the new fibre suffered from certain defects, such as inflammability and liability to damage by