beet, carrot and other roots were identical with cane sugar. The sugars obtained from honey were investigated by Lowitz and Proust, and the latter decided on three species: (ι) cane sugar, (2) grape sugar, and (3) fruit sugar; the first has the formula C12H22O11, the others C6H12O6. This list has been con­siderably developed by the discovery of natural as well as of synthetic sugars.

It is convenient to divide the sugars into two main groups: monosaccharoses (formerly glucoses) and disaccharoses (formerly saccharoses). The first term includes simple sugars containing two to nine atoms of carbon, which are known severally as bioses, trioses, tetroses, pentoses, hexoses, &c.; whilst those of the second group have the formula C12H22O11 and are characterized by yielding two monosaccharose molecules on hydrolysis. In addition tri saccharoses are known of the formula C18H22O16; these on hydrolysis yield one molecule of a monosaccharose and one of a disaccharose, or three of a monosaccharose. It is found also that some mono­saccharoses behave as aldehydes whilst others contain a keto group ; those having the first character are called *aldoses,* and the others *ketoses.* All sugars are colourless solids or syrups, which char on strong heating; they are soluble in water, forming sweet solutions but difficultly soluble in alcohol. Their solutions are optically active, *i.e.* they rotate the plane of polarized light; the amount of the rotation being dependent upon the concentration, temperature, and, in some cases, on the age of the solution (cf. Glucose). The rotation serves for the estimation of sugar solutions (saccharimetry). They are neutral to litmus and do not combine with dilute acids or bases; strong bases, such as lime and baryta, yield saccharates, whilst, under certain conditions, acids and acid anhydrides may yield esters. Sugars are also liable to fermentation.@@1 Our knowledge of the chemical structure of the monosaccharoses may be regarded as dating from 1880, when Zincke suspected some to be ketone alcohols, for it was known that glucose and fructose, for example, yielded penta-acetates, and on reduction gave hexahydric alcohols, which, when reduced by hydriodic acid, gave normal and secondary hexyliodide. The facts suggested that the six carbon atoms formed a chain, and that a hydroxy group was attached to five of them, for it is very rare for two hydroxy groups to be attached to the same carbon atom. The remaining oxygen atom is aldehydic or ketonic, for the sugars combine with hydrocyanic acid, hydroxy­lamine and phenylhydrazine. The correctness of this view was settled by Kiliani in 1885. He prepared the cyanhydrins of glucose and fruotose, hydrolysed them to the corresponding oxy-acids, from which the hydroxy groups were split out by reduction; it was found that glucose yielded normal heptylic acid and fructose methylbutylacetic acid; hence glucose is an aldehyde alcohol, CH2OH∙(CH∙OH)4∙CHO, whilst fructose is a ketone alcohol CH2OH∙(CH∙OH)4∙CO∙CH2OH.@@2 Kiliani also showed that arabinose, CiHι2O9, a sugar found in cherry gum, was an aldopentose, and thus indicated an extension of the idea of a “ sugar.”

Before proceeding to the actual synthesis of the sugars, it is advisable to discuss their decompositions and transformations.

1. *Cyanhydrins.—*The cyanhydrins on hydrolysis give mono­carboxylic acids, which yield lactones; these compounds when reduced by sodium amalgam in sulphuric acid solution yield a sugar containing one more carbon atom. This permits the formation of a higher from a lower sugar (E. Fischer)

CH2OH ch2oh CHsOH ch2oh

CH·OH CH·OH ∕CH CH·OH

(CH∙OH)2 → (CH∙OH)2 → ∕(CH∙OH)2 → (CH∙OH)2

CHO CH·OH υ∖ CH·OH CH·OH

CN ×CO CHO

Pentose → Cyanhydrin → Lactone → Hexose.

2. *Oximes.—*The oximes permit the reverse change, *i.e.* the passage from a higher to a lower sugar. Wohl forms the oxime and converts it into an acetylated nitrile by means of acetic anhydride and sodium acetate; ammoniacal silver nitrate solution removes hydrocyanic acid and the resulting acetate is hydrolysed by acting with ammonia to form an amide, which is finally decomposed with sulphuric acid.

ch2oh ch2oh ch2oh ch2oh

(CH·OH), → (CH·OH), → (CH·OH), → (CH·OH),

CH·OH CH·OH CH·OH CHO

CHO CH :NOH CN

Hexose → Oxime → Nitrile → Pentose.

Ruff effects the same change by oxidizing the sugar to the oxy-acid,

and then further oxidizing this with Fenton’s reagent, *i.e.* hydrogen peroxide and a trace of a ferrous salt :

C4H,O4(CH∙OH)∙CHO→C4H9O4(CH∙OH)∙CO2H→C4HaO4∙CHO

Hexose → Acid → Pentose.

3. *Phenylhydrazine Derivatives.—*Fischer found that if one mole­cule of phenylhydrazine acted upon one molecule of an aldose or ketose a hydrazone resulted which in most cases was very soluble in water, but if three molecules of the hydrazine reacted (one of which is reduced to ammonia and aniline) insoluble crystalline substances resulted, termed *osazones,* which readily characterized the sugar from which it was obtained.

R R R

CH·OH → CH·OH → C:N·NHPh

CHO CH:N·NHPh. CH:N·NHPh.

Aldose → Hydrazone → Osazone;

R R R

CO → C:N·NHPh. → C:N·NHPh

CH2OH CH2OH CH :N·NHPh.

Ketose → Hydrazone → Osazone.

On warming the osazone with hydrochloric acid the phenylhydra­zine residues are removed and an *osone* results, which on reduction with zinc and acetic acid gives a ketose.

R R R

C:N·NHPh. → CO — CO

CH:N·NHPh. CHO CH2OH

Osazone → Osone → Ketose.

A ketose may also be obtained by reducing the osazone with zinc and acetic to an *osamine,* which with nitrous acid gives the ketose :

R R R

C:N·NHPh. → CO → CO

CH:N·NHPh. CH2NH2 CH2OH.

Osazone → Osamine → Ketose.

These reactions permit the transformation of an aldose into a ketose; the reverse change can only be brought about by reducing the ketose to an alcohol, and oxidizing this compound to an aldehyde. It is seen that aldoses and ketoses which differ stereochemically in only the two final carbon atoms must yield the same osazone; and since *d*-mannose, *d*-glucose, and *d*-fructose do form the same osazone (*d*-glucosazone) differences either structural or stereochemical must be placed in the two final carbon atoms.@@3

It may here be noticed that in the sugars there are asymmetric carbon atoms, and consequently optical isomers are to be expected. Thus glucose, containing four such atoms, can exist in 16 forms; and the realization of many of these isomers by E. Fischer may be regarded as one of the most brilliant achievements in modern chem­istry. The general principles of stereochemistry being discussed in Stereoisomerism (*q.v*.), we proceed to the synthesis of glucose and fructose and then to the derivation of their configurations.

In 1861 Butlerow obtained a sugar-like substance, methylenitan, by digesting trioxymethylene, the solid polymer of formaldehyde, with lime. The work was repeated by O. Loew, who prepared in 1885 a sweet, unfermentable syrup, which he named formose, C6H12O6, and, later, by using magnesia instead of lime, he obtained the fermentable methose. Fischer showed that methose was identical with the α-acrose obtained by himself and Tafel in 1887 by decomposing acrolein dibromide with baryta, and subsequently prepared by oxidizing glycerin with bromine in alkaline solution, and treating the product with dilute alkali at 0°. Glycerin appears to yield, on mild, oxidation, an aldehyde, CH2OH∙CH(OH)∙CHO, and a ketone, CH2OH∙CO∙CH2OH, and these condense as shown in the equation :

CH2OH∙CH(OH)∙CHO+CH2OH∙CO∙CH2OH= CH2OH∙CH(OH)∙CH(OH)∙CH(OH)∙CO2CH2OH+H2O.

The osazone prepared from α-acrose resembled most closely the glucosazone yielded by glucose, mannose, and fructose, but it was optically inactive; also the ketose which it gave after treatment with hydrochloric acid and reduction of the osone was like ordinary fructose except that it was inactive. It was surmised that α-acrose was a mixture of dextro and laevo fructose, a supposition which was proved correct by an indirect method. The starting point was ordinary(d)mannite (mannitol),C6H14O6, a naturally occur­ring hexahydric alcohol, which only differed from α-acntol, the alcohol obtained by reducing α-acrose, with regard to optical activity. Mannite on oxidation yields an aldose, mannose, C6H12O6, which

@@@1 See Fermentation; and for the relation of this property to structure see Stereoisomerism.

@@@2 These formulae, however, require modification in accordance with the views of Lowry and E. F. Armstrong, which postulate a γ oxidic structure (see Glucose). This, however, does not disturb the tenor of the following arguments.

@@@1 To distinguish the isomerides of opposite optical activity, it is usual to prefix the letters *d-* and *l*-, but these are used only to indicate the genetic relationship, and not the character of the optical activity ; ordinary fructose, for example, being represented as d-fructose—- although it exercises a laevorotatory power—because it is derived from d-glucose.