on further oxidation gives a mannonic acid, C5He(OH)5·CO2H; this acid readily yields a lactone. Also Kiliani found that the lactone derived from the cyanhydrin of natural arabinose (laevo) was identical with the previous lactone except that its rotation was equal and opposite. On mixing, the eslactones and reducing (*d*+*l*)-mnanitol was obtained, identical with α-acritol. . A separation of α-acrose was made by acting with beer yeast, which destroyed the ordinary fructose and left *l*-fructose which was isolated as its osazone. Also (d+*l*) mannonic acid can be split into the *d* and *I* acids by fractional crystallization of the strychnine or brucine salts. The acid yields, on appropriate treatment, *d*-mannose and *d*-mannite. Similarly the *l* acid yields the laevo derivatives. .

The next step was to prepare glucose. This was effected in­directly. The identity of the formulae and osazones of *d*-mannose and *d*-glucose showed that the stereochemical differences were situated at the carbon atom adjacent to the aldehyde group. Fischer applied a method indicated by Pasteur in converting, dextro into laevo-tartaric acid; he found that both *d*-mannonic and *d*-gluconic acids (the latter is yielded by glucose on oxidation) were mutually convertible by heating with quinoline under pressure at 140°. It was then found that on reducing the lactone of the acid obtained from *d*-mannonic acid, ordinary glucose resulted.

Fischer's α-acrose therefore led to the synthesis of the dextro and laevo forms of mannose, glucose and fructose; and these substances have been connected synthetically with many other sugars by means of his cyanhydrin process, leading to higher sugars, and Wohl and Ruff's processes, leading to lower sugars. Certain of these relations are here summarized (the starting substance is in italics) :—

/-Glucose ÷— *l-arabinose* —> /-mannose —> /-mannoheptose; glucononose ÷- α-gluco-octosc ÷- a-glucoheρtose <— *d-glucose —>* ß-glucoheptose —> 0-gluco-octose ;

*d-mannose—>* d-mannoheρtose->manno-oct ose—>mannononosc; *d-glucose —>* d-arabinose —> d-erythrose.

*l-glucose~*⅛ δ-arabinose —⅛ /-erythrose.

Their number is further increased by spatial inversion of the dicarb­oxylic acids formed on oxidation, followed by reduction; for example: *d-* and *l*-glucose yield *d*-and *l*-gulose; and also by Lobry de Bruyn and Van Ekenstein’s discovery that hexoses are transformed into mixtures of their isomers when treated with alkalis, alkaline earths, lead oxide, &c.

*Monosaccharoses.*

*Bíose.—*The only possible biose is glycollic aldehyde, CHO∙CH2OH, obtained impure by Fischer from bromacetaldehyde and baryta water, and crystalline by Fenton by heating dihydroxymaleic acid with water to 60°. It polymerizes to a tetrose under the action of sodium hydroxide.

*Trioses.—*The trioses are the aldehyde and ketone mentioned above as oxidation products of glycerin. Glyceric aldehyde, CH2OH∙CH(OH)∙CHO, was obtained pure by Wohlon oxidizing acrolein acetal, CH2∙CH(OC2H5)2, and hydrolysing. Although containing an asymmetric carbon atom it has not been resolved. The ketone, dihydroxyacetone, CH2OH∙CO∙CH2OH, was obtained by Piloty by condensing formaldehyde with nitromethane, reducing to a hydroxylamino compound, which is oxidized to the oxime of dihydroxyacetone; the ketone is liberated by oxidation with bromine 3H∙CHO + CH,NO2 → (CH20H)jC∙NO2 → (CH1OH)sC∙NH OH → (CH2OH)2C : NOH→(CH2OH)2CO. The ketone is also obtained when Bertrand’s *sorbose bacterium* acts on glycerol; this medium also acts on other alcohols to yield ketoses; for example: erythrite gives erythrulose, arabite arabinulose, mannitol fructose, &c.

*Tetroses.—*Four active tetroses are possible, and three have been obtained by Ruff and Wohl from the pentoses. Thus Wohl pre- pared *l*-threose from *l*-xylose and *l*-erythrose from *l*-arabinose, and Ruff obtained *d-* and *l*-erythrose from *d-* and *l*-arabonic acids, the oxidation products of *d-* and *l*-arabinoses. Impure inactive forms result on the polymerization of glycollic aldehyde and also on the oxidation of erythrite, a tetrahydric alcohol found in some lichens. *d*-Erythrulose is a ketose of this series.

*Pentoses.—*Eight stereoisomeric pentaldoses are possible, and six are known : *d-* and, *l*-arabinose, *d-* and *l*-xylose, *l*-ribose, and *l*-lyxose. Scheibler discovered *l*-arabinose in 1869, and regarded it as a glucose; in 1887 Kiliani proved it to be a pentose, *d-* Arabi nose is obtained from *l*-glucose by Wohl’s method. *l*-Xylose was dis­covered by Koch in 1886; its enantiomorph is prepared from d-gulose by Wohl's method. *l*-Ribose and *d-*lyxose are prepared by inversion from *l*-arabinose and *l*-xylose; the latter has also been obtained from *l*-galactose. We may notice that the pentoses differ from other sugars by yielding furfurol when boiled with hydrochloric acid. Rhamnose or isodulcite, a component of certain glucosides, fucose, found combined in seaweeds and chinovose, present as its ethyl ester, chinovite, in varieties of quina-bark, are methyl pentoses. /-Arabinulose obtained from arabite and Bertrand’s *sorbium bacterium* is a ketose.

*Hexoses.—*The hexoses may be regarded as the most important sub-division of the monosaccharoses. The reader is referred to Glucose and Fructose for an account of these substances. The next important aldose is mannose. *d*-Mannose, first prepared by oxidizing *d*-mannite, found in plants and manna-ash *(Fraxinus ornus),* was obtained by Tollens and Gans on hydrolysing cellulose and by Reis from seminine (reserve cellulose), found in certain plant seeds, *e.g.* vegetable ivory. *l*-Mannose is obtained from *l*-mannonic acid. Other forms are : *d-* and *l*-gulose, prepared from the lactones of the corresponding gulonic acids, which are obtained from *d-* and *l*-glucose by oxidation and inversion; *d-* and ∕-idose, obtained by inverting with pyridine *d-* and *l*-guíonic acids, and reducing the resulting idionic acids; *d-* and *l*-galactose, the first being obtained by hydrolysing milk sugar with dilute sulphuric acid, and the second by fermenting inactive galactose (from the reduction of the lactone of *d,* ∕-galactonic acid) with yeast; and *d-* and *l*-talose obtained by inverting the galactonic acids by pyridine into *d-* and *l*-talonic acids and reduction. Of the ketoses, we notice «/-sorbose, found in the berries of mountain-ash, and *d*-tagatose, obtained by Lobry de Bruyn and van Ekenstein on treating galactose with dilute alkalis, talose and *l*-sorbose being formed at the same time. The higher sugars call for no special notice.

*Configuration of the Hexaldoses.@@1—*The plane projection of molecular structures which differ stereochemically is discussed under Stereo­isomerism; in this place it suffices to say that, since the terminal groups of the hexaldose molecule are different and four asymmetric carbon atoms are present, sixteen hexaldoses are possible; and for the hexahydric alcohols which they yield on reduction, and the tetrahydric dicarboxylic acids which they give on oxidation, only ten forms are possible. Employing the notation in which the molecule is represented vertically with the aldehyde group at the bottom, and calling a carbon atom + or - according as the hydrogen atom is to the left or right, the possible configurations are shown in the diagram. The grouping of the forms 5 to 10 with 11 to 16 is designed to show that the pairs 5, 11 for example become identical when the terminal groups are the same.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  | **11** | **12** | 13 | 14 | 15 | 16 |
|  |  |  |  | + | + | + | + | + | **-** |
|  |  |  |  | + | + | + | - | - | **+** |
|  |  |  |  | + | - | - | + | - | **-** |
|  |  |  |  | - | + | - | - | - | **-** |
| + | + | *-* | - | - | + | - | - | - | **-** |
| + | - | + | - | + | - | - | + | - | **-** |
| + | - | + | - | + | + | + | - | - | **+** |
| + | + | - | - | + | + | + | + | + | **-** |
| **I** | ***2*** | 3 | 4 | 5 | 6 | 7 | 8 | 9 | **10** |

We can now proceed to the derivation of the structure of glucose. Since both d-glucose and <∕-gulose yield the same active (*d*) saccharic acid on oxidation, the configuration of this and the corresponding /-acid must be sought from among those numbered 5-10 in the above table. Nos. 7 and 8 can be at once ruled out, however, as acids so constituted would be optically inactive and the saccharic acids are active. If the configuration of *d-*saccharic acid were given by either 6 or 10, bearing in mind the relation of mannose to glucose, it would then be necessary to represent d-mannosaccharic acid by either 7 or 8—as the forms 6 and 10 pass into 7 and 8 on changing the sign of a terminal group; but this cannot be done as mannosac­charic acid is optically active. Nos. 6 and 10 must, in consequence, also be ruled out. No. 5, therefore, represents the configuration of one of the saccharic acids, and No. 9 that of the isomeride of equal opposite rotatory power. As there is no means of distinguish­ing between the configuration of a dextro- and laevo-modification, an arbitrary assumption must be made. No. 5 may therefore be assigned to the d- and No. 9 to the *l*-acid. It then follows that *d*-mannose is represented by No. I, and *l*-mannose by No. 4, as man­nose. is produced by reversing the sign of the asymmetric system adjoining the terminal COH group.

It remains to distinguish between 5 and 11, 9 and 15 as representing glucose and gulose. To settle this point it is necessary to consider the configuration of the isomeric pentoses—arabinose and xylose— from which they may' be prepared. Arabinose being convertible into *l*-glucose and xylose into *l*-gulose, the alternative formulae to be considered are—

CH2(OH)---+COH

CH2(OH)+++-COH.

@@@1 The following account is mainly from H. E. Armstrong's article Chemistry in the 10th edition of this Encyclopaedia; the representa­tion differs from the projection of Meýer and Jacobsen.