CCXII.—*The Classification of the Sugars.*

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THE original classification of the normal forms of the sugars and their derivatives into the *d*- and *l*-series was that of Fischer (*Ber.*, 1894, **27**, 3208) and depended on their chemical relationship to naturally occurring (*d*-)glucose. The classification usually adopted to-day is that of Rosanoff (*J. Amer. Chem. Soc.*, 1906, **28**, 114) in which the configuration of the asymmetric group furthest removed from the aldehydic group is the deciding factor. A classification depending on the mean of the rotations of the α- and β-forms was put forward in an earlier paper (J., 1922, **121**, 2608).

Most sugars and their derivatives are obtainable in α- and β-forms, and the usually accepted distinctions between them are those given by the action of enzymes, the mode of preparation and the rate of hydrolysis of the glucosides. A different distinction has been given by Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 66) based on their rotations and on Fischer's classification into the *d*- and *l*-series. According to this, the α-form of a *d*-sugar has a more positive rotation than the β-form. In the case of arabinose, however, the two methods of distinction do not agree (Hudson, *J. Amer. Chem. Soc.*, 1924, **46**, 2591), the same being the case if Rosanoff's classification is used. It seems possible that the cause of the discrepancy lies in the classification into the *d*- and *l*-series being wrong.

It is suggested that, for the normal forms of the aldoses, the configuration of the middle group of the oxide ring (group 3) is the deciding factor in the classification into the *d*- and *l*-series. Naturally occurring arabinose therefore now belongs to the *d*- instead of to the *l*-series, and the α-forms of the *d*-sugars have more positive rotations than the β-forms for all known cases, as shown in the table below. In an earlier paper (J., 1923, **123**, 1404), it was suggested from a consideration of the rotations of the sugars that, in the α-form of the aldoses, groups 1 and 3 have opposite configurations. It was also shown that the configuration of group 3 determines the relative proportions of the two products formed by the cyanohydrin synthesis. This follows, since the configuration of group 2 in the main product is always the opposite of that of group 4, the latter being group 3 in the original sugar. This is also shown in the table below, in which the configurations are represented by + and — signs as suggested by Fischer (*Ber.*, 1894, **27**, 3189) and the *d*-sugars have been taken as those with a positive sign for group 3.

Sugar.	Configuration of sugar.				Specific rotation of sugar.			Configuration of main cyanohydrin product.				
	5.	4.	3.	2.	α.	Equil.	β.	6.	5.	4.	3.	2.
d-Glucose	—	—	+	—	100°	52°	20°	—	—	+	—	—
d-Mannose	—	—	+	+	30	14	—15	—	—	+	+	—
d-Galactose......	—	+	+	—	140	80	51	—	+	+	—	—
d-Arabinose ...		+	+	—	150	105	76		+	+	—	—
d-Xylose		—	+	—	92	19	—20		—	+	—	—
d-*iso*Rhamnose	—	—	+	—	73	30	—					
l-Ribose		—	—	—					—	—	—	+
l-Rhamnose ...	+	+	—	—	—7	9	54	+	+	—	—	+
l-Fucose	±	—	—	+	—112	—77	—					

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