

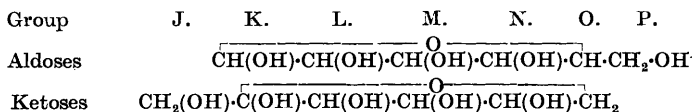
CCCLXX.—*The Classification of the Sugars. Part II.*

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It has been shown (J., 1923, **123**, 1404; 1926, 1629) that, for the normal forms of the aldoses, the configuration of the middle group of the oxide ring plays an important part in the division into the *d*- and *l*-series, in the classification of the α - and β -forms, and also in determining the configuration of the main product of the cyanohydrin synthesis. It is now proposed to amplify the previous work, dealing at present only with the normal forms of the sugars, for which the term pyranose has been suggested (Goodyear and Haworth, J., 1927, 3136).

According to the present system of nomenclature for the sugars, similar groups in the aldoses and ketoses are given differing numbers. In order to simplify the comparison of these two types of sugar, it is suggested that the carbon groups in the oxide ring of the pyranoses

should be lettered K, L, M, N, and O, group K being the reducing group and group M the middle group of the three secondary alcohol groups in the ring. When there are other carbon groups at either end of the chain, they are given adjacent letters of the alphabet. This is shown below for the hexoses :



This nomenclature being applied to the generalisations found previously, and the ketoses being included, group M in the *d*-pyranoses will have the same configuration as in ordinary glucose, and in the α -forms the configurations of groups K and M will be opposite. Owing to the rotational effect of group K, the α -forms of the *d*-pyranoses will have a higher positive rotation than the β -forms.

On comparing their configurations with that of ordinary *d*-glucose, it will be seen that fructose and α -glucoheptose belong to the *l*-series, and not to the *d*-series as they do according to the usually accepted views. An examination of the chemical evidence shows that these two sugars resemble arabinose (J., 1926, 1629 ; Hudson, *J. Amer. Chem. Soc.*, 1924, **46**, 2591) in that the α - and β -forms are respectively the β - and α -forms as determined by Hudson's rule (*J. Amer. Chem. Soc.*, 1909, **31**, 66). For fructose, see Parcus and Tollens (*Annalen*, 1890, **257**, 160), Purdie and Paul (J., 1907, **91**, 289), Fischer (*Ber.*, 1895, **28**, 1145), Hudson and Brauns (*J. Amer. Chem. Soc.*, 1916, **38**, 1216), Brauns (*ibid.*, 1920, **42**, 1846), and Schlubach and Schröter (*Ber.*, 1928, **61**, 1216). For α -glucoheptose, see Fischer (*Annalen*, 1892, **270**, 64 ; *Ber.*, 1895, **28**, 1145) and Hudson (*J. Amer. Chem. Soc.*, 1925, **47**, 268).

The configurations and specific rotations of the three sugars are as below, the configurations being represented by + and - signs as suggested by Fischer (*Ber.*, 1896, **27**, 3189) :

Sugar.	L.	Configuration.			P.	α .	Equil.	β .
		M.	N.	O.				
<i>d</i> -Glucose	-	+	-	-	-	111°	52°	19°
<i>l</i> - α -Glucoheptose ...	-	-	+	-	-	-28	-20	45
<i>l</i> -Fructose	+	-	-	-	-	-133	-92	-21

The Cyanohydrin Synthesis.—It was shown in an earlier paper that the configuration of group 2 in the main product of the cyanohydrin synthesis is the opposite of that of group 4, the latter being

group M in the original sugar. The following examples can be added :

Sugar.	Main product.	Configuration.					Reference.
		2	3	4	5	6	
Lyxose	Galactonic acid	-	+	+	-		Fischer and Ruff, <i>Ber.</i> , 1900, 33 , 2142.
Gulose	α -Gulo-heptonic acid	+	-	-	+	-	La Forge, <i>J. Biol. Chem.</i> , 1920, 41 , 251.
α -Manno-heptose	$\alpha\alpha$ -Manno-ctonic acid	-	-	+	+	-	Peirce, <i>J. Biol. Chem.</i> , 1915, 23 , 327.
Fructose	Fructose-carboxylic acid	+	+	-	-		Kilian, <i>Ber.</i> , 1922, 55 , 2817.

Rhodoose is, however, an apparent exception (Krauz, *Ber.*, 1910, **43**, 482; Votoček, *ibid.*, p. 469). The configurations suggested by Krauz for α - and β -rhodeohexose are, however, the opposite of those deduced from the rotations of the amides of α - and β -rhodeohexonic acids obtained by him, by applying Hudson's rule (*J. Amer. Chem. Soc.*, 1918, **40**, 813). On the assumption that no abnormalities occur, the configurations can be determined for the higher sugars, and from these the series (*d* or *l*) to which they belong :

Sugar.	Configuration.							
	L.	M.	N.	O.	P.	Q.	R.	S.
<i>aa-d</i> -Rhamnoheptose	+	+	-	-	+	+		
<i>aa-l</i> -Gluco-octose	+	-	-	+	-	-		
<i>aaa-d</i> -Glucononose ...	+	+	-	-	+	-	-	
<i>aaaa-d</i> -Glucodecose ...	-	+	+	-	-	+	-	-
<i>aa-l</i> -Galactose	+	-	-	+	+	-		
<i>aaa-l</i> -Mannonose	+	-	-	+	+	-	-	
<i>a-l</i> -Rhodeohexose	-	-	+	+	-			

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