263. *Ionophoresis of Carbohydrates. Part V.* Reaction of the Methyl Fructofuranosides and Fructopyranosides, and of Related Compounds, with Borate Ions.*

By A. B. Foster.

The reaction of a series of glycofuranosides and glycopyranosides with borate ions has been measured. The structures of the methyl α- and β-D-fructofuranoside and methyl α- and β-D-fructopyranoside allocated on the basis of borate-ion interactions (M_G values) correspond with those allocated on the basis of specific optical rotations.

Information on the structure of carbohydrates has been gained in certain instances [1,2] by observing their reaction with borate ions in alkaline media. The reaction of carbohydrates with borate ions in aqueous boric acid at pH 5 has been extensively studied by Böeseken [3] using conductimetric methods. However, in alkaline media, borate-ion interactions are intensified [4] and new types of interactions have been observed.[5] The M_G value [1] has been adopted in these investigations as a convenient index of borate-ion interaction: it may be determined for a given substance by zone electrophoresis [6] (ionophoresis) on paper by using the enclosed-strip technique.[7]

Recent chromatographic techniques [8,9] have made available a number of new methyl glycofuranosides and through the courtesy of Professor E. Berner samples have been made available for ionophoresis.

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* Part IV, *J.*, 1956, 4311.

[1] Foster, *J.*, 1953, 982.

[2] (*a*) Foster and Stacey, *Chem. and Ind.*, 1953, 279; (*b*) Foster, *ibid.*, 1953, 591; (*c*) Foster, Overend, Stacey, and Vaughan, *J.*, 1953, 3308; (*d*) Bera, Foster, and Stacey, *J.*, 1956, 4531.

[3] Böeseken, *Adv. Carbohydrate Chem.*, 1949, **4**, 189.

[4] Consden and Stanier, *Nature*, 1952, **169**, 783.

[5] See, *e.g.*, Foster and Stacey, *J.*, 1955, 1778.

[6] Flodin and Tiselius, *Adv. Protein Chem.*, 1953, **8**, 461.

[7] Foster, *Chem. and Ind.*, 1952, 1050.

[8] Augestad, Berner, and Weigner, *ibid.*, 1953, 376.

[9] Augestad and Berner, *Acta Chem. Scand.*, 1954, **8**, 251.

From the M_G values recorded in the Table it is seen that both methyl α- and β-D-arabofuranoside have a definite though a very weak reaction with borate ions. Three possibilities exist, in these glycofuranosides, for borate-ion interactions, involving the 2 : 3-, 2 : 5-, and 3 : 5-hydroxyl groups. (The relative stereochemical disposition of all three hydroxyl groups precludes the formation of a " tridentate " complex.[10]) The 2 : 3-hydroxyl groups are *trans*-related and are effectively fixed in space because they are attached to the almost completely rigid furan ring;[11] the O–O distance is greater than that in *cyclo*hexane-*trans*-1 : 2-diol which does not react with borate ions.[2b] A seven-membered ring would result from a borate-ion reaction with the 2 : 5-hydroxyl groups and the formation of such a complex would seem unlikely since butane-1 : 4-diol, which would yield a similar complex, has a zero M_G value.[12] The formation of a borate complex spanning the 3 : 5-hydroxyl groups would necessitate the formation of a somewhat distorted six-membered ring and would seem to be the most likely of the three possibilities considered. Evidence which supports this view is the observed [13] small, but definite, difference in M_G values of adenosine-2′ and -3′ phosphate (1·06 and 1·02 respectively) which could be due to the former's acquiring extra negative charge by reaction of borate ions with the 3′ : 5′-hydroxyl groups. It is of interest that the weak reaction of structures of the type (I) and (II) with borate ions has been of value [2d] in the determination of the structure of 2 : 5-anhydro-D-mannitol.

cis-Arrangement of the hydroxymethyl and vicinal hydroxyl group as in methyl α- and β-D-xylofuranoside permits a much stronger reaction with borate ions, as indicated by the M_G values in the Table. The M_G values of methyl α- and β-D-fructofuranoside (0·60 and 0·04 respectively) are consistent with the presence of, respectively, vicinal *cis*- and *trans*-related hydroxymethyl and hydroxyl groups at positions 2 and 3, *i.e.*, the compounds have the structures (V) and (VI).

Thus the structures allocated to the fructofuranosides on the basis of their M_G values are in agreement with those allocated on the basis of specific optical rotations (cf. Pigman and Goepp [14]).

The M_G values of the D-gluco- and D-galacto-furanoside derivatives in the Table show, as expected, a stronger reaction with borate ions in the former series where the non-protonic groups on $C_{(3)}$ and $C_{(5)}$ are *cis*-related (cf. McPherson and Percival's observations [15] on the influence of these furanosides on the conductivity of boric acid). The M_G values of the D-galactofuranose derivatives are higher than would be expected from the fact that propane-1 : 2-diol has an M_G value of 0·2 and the assumption that only the 5 : 6-hydroxyl groups in these derivatives react with borate ions. Other, as yet undefined, borate-ion interactions appear to be operating here.

M_G values of some glycofuranosides and pyranosides.

	M_G value		M_G value
Me α-D-arabofuranoside (I)	0·035	Me α-D-galactofuranoside	0·41
Me β-D-arabofuranoside (II)	0·035	Me β-D-galactofuranoside	0·31
Me α-D-xylofuranoside (III)	0·56	1 : 4-Anhydro-D-galactitol	0·47
Me β-D-xylofuranoside (IV)	0·33	Me α-D-fructopyranoside [c] (VII)	0·71
Me α-D-fructofuranoside [a] (V)	0·60	Me β-D-fructopyranoside [d] (VIII)	0·59
Me β-D-fructofuranoside [b] (VI)	0·04	Me α-D-mannopyranoside (IX)	0·42
Me α-D-glucofuranoside	0·73	Me β-D-gulopyranoside (X)	0·72
1 : 2-*O*-*iso*Propylidene-α-D-glucofuranose	0·73		

Physical constants of the fructose derivatives (personal communication from Professor E. Berner): (*a*) m. p. 81°, $[\alpha]_D$ +93° in H_2O; (*b*) syrup, $[\alpha]_D$ −48° in H_2O; (*c*) syrup, $[\alpha]_D$ +80° in EtOH; (*d*) m. p. 120°, $[\alpha]_D$ −173° in H_2O.

Because of a lack of suitable compounds it has not been possible to measure directly

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[10] Angyal and McHugh, *Chem. and Ind.*, 1956, 1147.

[11] Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 1.

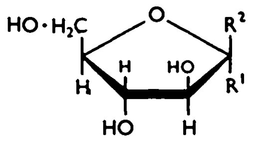
[12] Frahn and Mills, *Chem. and Ind.*, 1956, 578.

[13] Burke and Foster, *ibid.*, 1955, 94.

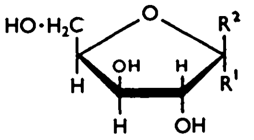
[14] Pigman and Goepp, " Carbohydrate Chemistry," Academic Press, New York, 1948, p. 80.

[15] Macpherson and Percival, *J.*, 1937, 1920.

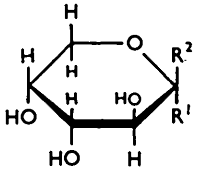
the reaction of borate ions with vicinal *cis*-related hydroxyl and hydroxymethyl groups in pyran derivatives but it may be deduced that they react more strongly than with the corresponding *trans*-related groups. (The reaction of the latter grouping with borate ions has been noted in Part II of this series.) Thus borate ions may react separately at two points in methyl β-D-gulopyranoside (X) and methyl α-D-mannopyranoside (IX), *viz.*, the *cis*-2 : 3-hydroxyl groups, and the hydroxymethyl and 4-hydroxyl groups which are *trans*-related in the latter and *cis*-related in the former. On the reasonable assumption that the contribution to the negative charge of the derivatives (IX) and (X) conferred by reaction of the 2 : 3-hydroxyl groups with borate ions is similar, the much greater M_G value of the D-gulose derivative (X) (see Table) probably originates in a readier reaction of the 4 : 6-hydroxyl groups with borate ions in this than in the D-mannose derivative (IX). Although the reaction of the 4 : 6-hydroxyl groups in the D-mannose derivative (IX) is sterically hindered by the glycosidic methoxyl group (Part II) this can account for only a fraction of the difference in the M_G values of methyl α-D-mannopyranoside and β-D-gulopyranoside.



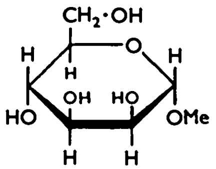
(I) R^1 = OMe, R^2 = H
(II) R^1 = H, R^2 = OMe
(V) R^1 = OMe, R^2 = CH_2·OH
(VI) R^1 = CH_2·OH, R^2 = OMe



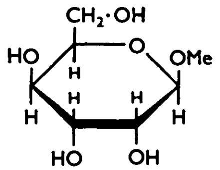
(III) R^1 = OMe, R^2 = H
(IV) R^1 = H, R^2 = OMe



(VII) R^1 = OMe, R^2 = CH_2·OH
(VIII) R^1 = CH_2·OH, R^2 = OMe



(IX)



(X)

The higher M_G value of methyl α-D-fructopyranoside (VII) than of the β-anomer (VIII) is consistent with the presence of respectively *cis*- and *trans*-related 3-hydroxyl and 2-hydroxymethyl groups in the two compounds. It is of interest that methyl β-D-gulopyranoside (X) and α-D-fructopyranoside (VII) which have closely related structures, with respect to the steric disposition of their hydroxyl groups, also have closely similar M_G values.

From a knowledge of the M_G values of the methyl D-fructofuranosides (V) and (VI) the observed low M_G value (< 0·05) for inulin is not unexpected. A similar low M_G value would be predicted for levan.

EXPERIMENTAL

The apparatus and technique employed in ionophoresis have been previously described.[7] Ionophoreses were performed on Whatman No. 3 paper in sodium borate [16] at pH 10 under potential gradients of 20—40 v/cm. Non-reducing carbohydrates were detected by means of ammoniacal silver nitrate.[17]

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[16] Foster, Newton-Hearn, and Stacey, *J.*, 1956, 30.
[17] Hough, *Nature*, 1950, **165**, 400.