403. *Investigations on the Configuration of Carbohydrates by Conductivity Measurements in Boric Acid Solution.*

By H. T. Macpherson and E. G. V. Percival.

Böeseken's conclusions on the configuration of α- and β-*d*-glucose are confirmed, since conductivity and viscosity experiments with glucose, α-methylglucoside, and various methylated glucose derivatives make it clear that the only hydroxyl groups in glucose having any effect on the conductivity of a boric acid solution are those on C_1 and C_2. By using 3 : 4 : 6-trimethyl α-mannopyranose, the configuration is shown to be *trans*- with respect to the hydroxyl groups on C_1 and C_2, in contradistinction to Böeseken's results for β-mannose.

A striking elevation of conductivity is found for α-methylmannofuranoside, which is attributed to the orientation of the hydroxyl groups, four being situated in close proximity to one another; γ-methylglucoside, where three hydroxyl groups are close to one another, gives a lower elevation, and γ-methylgalactoside a depression. The behaviour of α-*l*-sorbose appears to be anomalous.

In a series of papers during 25 years Böeseken and his co-workers developed a method by means of which the structure of α-*d*-glucose was indicated to be of the *cis*-configuration with reference to the hydroxyl groups on C_1 and C_2. This conclusion was derived from the fact that α-glucose exhibited a higher conductivity than β-glucose in boric acid, and also that during mutarotation the conductivity of the α-glucose–boric acid solution fell, and that of the β-glucose–boric acid rose, to an intermediate equilibrium value (*Ber.*, 1913, **46**, 2612). From these facts Böeseken considered that complex formation occurred between boric acid and the hydroxyl residues on C_1 and C_2 in the case of α-glucose but not β-glucose. Although other methods of determining configuration, such as optical calculations (Freudenberg, Helferich, and Winkler, *Z. physiol. Chem.*, 1932, **209**, 270), *X*-ray studies (Cox *et al.*, J., 1932, 138, *et seq.*), and methods depending on differences of reactivity (Micheel and Micheel, *Ber.*, 1930, **63**, 386; Vavon, *Bull. Soc. chim.*, 1931, **49**, 997, 1011), have been elaborated, it seemed to us that this elegant method, if substantiated, might be of service particularly with regard to the structure of dissolved molecules.

It must be borne in mind, however, that in a molecule such as glucose with five free hydroxyl groups, other possibilities of combination with boric acid exist. Irvine and Steele (J., 1915, **107**, 1221) recognised this and examined methylated glucoses, and on the basis of a considerable elevation in conductivity following an initial depression for tetramethyl glucopyranose and an elevation for tetramethyl methylglucoside in boric acid solution, concluded that the oxygen atom of the ring combined with water to form an oxonium hydrate, which in turn formed a complex, together with the hydroxyl group on C_1, with boric acid. Böeseken and Couvert (*Rec. trav. chim.*, 1921, **40**, 354) repeated this work on purer specimens and found that, instead of the rapid increase of conductivity in boric acid solution, the initial depression underwent little change. We have now confirmed this result and extended it to α-methylglucopyranoside, 2 : 3 : 6-trimethyl glucopyranose, 2 : 3 : 6-trimethyl methylglucopyranoside, and sucrose. In all these cases diminution of conductivity below the sum of the values for the sugar derivative alone and of the boric acid solution was observed with no appreciable increase on standing. Viscosity determinations indicated that the observed depression ran parallel to the relative viscosity, so the diminution in conductivity was not anomalous. Incidentally, it was shown that Einstein's equation (*Ann. Physik*, 1906, **19**, 289), according to which viscosity is a function of the volume of the dissolved phase for approximately spherical molecules, was obeyed by these substances.

It is clear, therefore, not only that the ring oxygen atom, whether in a pyranose or a furanose sugar, has no effect on the conductivity of a boric acid solution, but also that in the case of glucose, the only hydroxyl groups having a positive effect are those on C_1 and C_2. No increase in conductivity is observed unless both these hydroxyl groups are unsubstituted and in the *cis*-position to one another.

Although the change in conductivity during the mutarotation of glucose is explained, it is to be noted that α-methylglucoside depresses the conductivity of boric acid solution; β-glucose in boric acid solution, however, gives, not the expected depression, but an initial elevation of the same order as the difference between the initial conductivities of the α- and the β-glucose. It may be that this initial conductivity is due to the presence in solution of a small amount of a straight-chain aldehydic form, possibly present as the aldehydrol. Straight-chain polyhydroxy-compounds such as dulcitol and sorbitol have a strongly positive effect on the conductivity of boric acid solution (*ca.* 600 × 10^{-6} mho* in M/2-solution), and it was found that glucose diethylmercaptal also had a strong positive effect (176 in M/10-solution).

The case of mannose is of interest since the earlier conductivity results indicate β-*d*-mannose to be a *trans*-form on the basis of a rise in conductivity during mutarotation, contrary to the accepted views for the configuration of this sugar. This case is complicated by the difficulty of securing β-mannose sufficiently pure for conductivity determinations, although our result for β-mannose is opposed to that of Böeseken and Couvert (*Rec. trav. chim.*, 1921, **40**, 370) in that we found a fall in conductivity. This result was supported, however, by using 3 : 4 : 6-trimethyl α-*d*-mannose (Bott, Haworth, and Hirst, J., 1930, 1395), in which any possibility of combination with boric acid at positions other than those under investigation is precluded. An initial depression was observed, in harmony with the results for the methylated glucose derivatives, and in agreement with viscosity determinations, but this depression gradually became less, parallel with the mutarotation, which at once confirms our observation on β-mannose and agrees with the present conception of the structure of this sugar. It is noteworthy that the change in conductivity is relatively small (this depends on the proportion of α- and β-forms at equilibrium) and that the relatively high initial value as found for β-glucose is absent.

α-*l*-Rhamnose suffered an elevation of conductivity during mutarotation, which agrees with the view that the hydroxyl groups on C_1 and C_2 are *trans*-.

Striking results were obtained with furanosides: γ-methylgalactoside (I) showed a depression of conductivity (12 gemmhos) (cf. α-methylglucopyranoside), but γ-methylglucoside (II) gave an elevation of 110 and α-methylmannofuranoside (III) an elevation of 3350. (These results are for M/2-solutions.) The result for the galactofuranoside reveals that the $\cdot CH(OH)\cdot CH_2\cdot OH$ group alone has no positive influence on the conductivity in this case. By comparison with ethylene glycol, which shows a depression, this is only to be expected, since this group, being a side chain, is permitted complete

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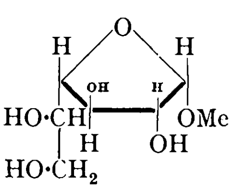
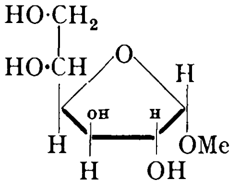
* All conductivities are subsequently given in terms of 10^{-6} mho.

freedom as to the relative positions of the hydroxyl groups, which will naturally incline to repel one another.

An examination of models, however, reveals that the glucofuranoside has a hydroxyl group in close proximity to the CH(OH)·CH_2·OH group, giving three hydroxyl residues near to one another. For the α-methylmannofuranoside we have two hydroxyl groups within easy reach of the CH(OH)·CH_2·OH group and on the same side of the ring plane.



(I.)



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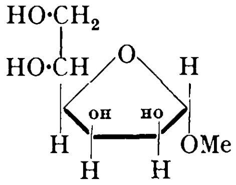


(III.)

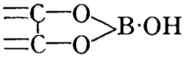
We thus have four hydroxyl groups as in erythritol, but here there is much less freedom of movement. In this case there is an accumulation of hydroxyl groups but the conditions are so complex that it is not yet possible to advance any definite hypothesis to account for the increase in conductivity.

Comparable with the elevation given by α-methylmannofuranoside is that of a α-*l*-sorbose, *viz.*, 2159 gemmhos in M/2-solution (cf. Böeseken and Leefers, *Rec. trav. chim.*, 1935, **54**, 865, who found 230 for M/10-solution). β-*d*-Fructose also gives a considerable elevation (703 in M/2-solution), but an examination of the ring structures for these ketoses fails to reveal the reason for the great difference between them. The fact that sorbose does not mutarotate might suggest that this sugar exists in solution in the keto-form, but other evidence does not favour such a view, and the question must be postponed for further study.

Rotation experiments have been carried out on α- and β-*d*-glucose, 3 : 4 : 6-trimethyl α-mannose, and α-methylmannofuranoside in both aqueous and boric acid solutions. No differences either in the equilibrium values or in the velocity of mutarotation were observed.

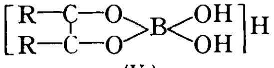
Consideration of the results for glycol, glycerol, erythritol, dulcitol, αβ-propylene glycol, and triethylene glycol shows that there is no very considerable increase in the conductivity of boric acid solution until four hydroxyl groups are present. Böeseken (*Rec. trav. chim.*, 1915, **34**, 96) showed that for pentaerythritol the elevation was about 6 times that observed for erythritol, and this appears to be due to the more rigid tetrahedral structure present in the former compound.

There has been some conflict of opinion as to whether or not the conductivity effects of polyhydroxy-compounds with boric acid are dependent on the formation of complexes (IV), as first proposed by van't Hoff, and since adopted by Böeseken and his co-workers. The extensive literature includes papers by Kolthoff (*Rec. trav. chim.*, 1925, **44**, 975), Bancroft and Davis (*J. Physical Chem.*, 1930, **34**, 2479), Henderson and Prentice (J., 1902, **81**, 658), Darmois (*J. Chim. physique*, 1926, **23**, 130, 649), Burgess and Hunter (J., 1929, 2838), Böeseken and Vermaas (*J. Physical Chem.*, 1931, **35**, 1477), Hermans (*Z. anorg. Chem.*, 1925, **142**, 83), and many others. The objections raised are chiefly based on the inability to isolate such complexes in the solid state from the highly conducting aqueous solutions. Nevertheless, Lowry (J., 1929, 2853) described a borotartaric acid, Hermans



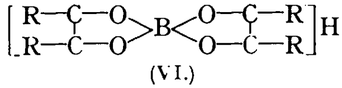
$\begin{array}{l}=\mathrm{C{-}O}\\ =\mathrm{C{-}O}\end{array}\!>\mathrm{B{\cdot}OH}$

(IV.)



$\left[\begin{array}{l}\mathrm{R{-}C{-}O}\\ \mathrm{R{-}C{-}O}\end{array}\!>\mathrm{B}<\!\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\end{array}\right]\mathrm{H}$

(V.)



$\left[\begin{array}{l}\mathrm{R{-}C{-}O}\\ \mathrm{R{-}C{-}O}\end{array}\!>\mathrm{B}<\!\begin{array}{l}\mathrm{O{-}C{-}R}\\ \mathrm{O{-}C{-}R}\end{array}\right]\mathrm{H}$

(VI.)

(*loc. cit.*) a disalicylboric acid, and Brigl and Grüner (*Annalen*, 1932, **495**, 60) a glucose diboric acid, although special conditions have to be used for the isolation of such derivatives. Hermans (*loc. cit.*) and Böeseken and Vermaas (*loc. cit.*) have suggested that the dissociable complexes may possess structures of the type (V) or (VI), according as one or two molecules of the hydroxy-compound are involved. In aqueous solution, however, it seems unreasonable that definite anhydrides such as this should be formed, and it is much more probable that the cyclic structure containing the boron atom is formed by a co-ordination process. Any such hypothesis must account for the increase in conductivity. By a mechanism analogous to the formation of BF_3,NH_3, boric acid may react with water to form the necessarily weak acid $\overset{+}{H}[\overset{-}{B}(OH)_4]$. If then the hydroxyl groups become associated with hydrogen atoms of the organic hydroxyl residue by means of hydroxyl bonds (Bernal and Megaw, *Proc. Roy. Soc.*, 1935, **151**, *A*, 384), which have recently been shown to be present in pentaerythritol (Llewellyn, Cox, and Goodwin, this vol., p. 883), it follows that as the number of these hydroxyl bonds around the boric acid is increased the negative charge on the central boron atom will be decreased, thus increasing the ease with which the hydrogen ion may be lost.

Examination of the results for α-*d*-galactose and α-methylgalactopyranoside suggests that the *cis*-hydroxyl groups at C_3 and C_4, by comparison with α-methylglucoside, have no (or, in the latter case only a slight) effect on the conductivity of boric acid solution. Böeseken (*Rec. trav. chim.*, 1921, **40**, 558) showed that whereas *cis-cyclo*pentane-1 : 2-diol gave a marked increase in conductivity, yet *cis-cyclo*hexane-1 : 2-diol gave a decrease. This can be understood when it is considered that the *cyclo*pentane ring is flat and the hydroxyl groups are in the same plane, but if the *cyclo*hexane ring is strainless, then the adoption of one or other of the Sachse–Mohr forms results in changes of the relative positions of both *cis*- and *trans*-hydroxyl groups and the alteration of conformation may perhaps account for the altered behaviour with boric acid. This can easily be seen by reference to models, and it is hoped that further investigation will lead to information on the conformation of the pyranose ring in solution.

EXPERIMENTAL.

Conductivity Experiments.

The Pyrex-glass conductivity vessel was specially constructed so that less than 1 c.c. of solution sufficed to cover the plates; the *polished* platinum electrodes were carried by the ground-in stopper, contact with the atmosphere being thereby excluded. Platinised plates were less satisfactory than polished platinum, which gave a sharp minimum for the solutions of low conductivity investigated in these experiments. The bridge, which was calibrated before use, was of the cylindrical type, wound with 3·6 m. of wire and divided into 1000 equal divisions, readings being taken to 0·25 of a scale division. A small induction coil and telephone were used in the usual manner in conjunction with standard variable resistances. The cell constant (0·4378) was determined with N/50-potassium chloride in conjunction with platinised electrodes, and with N/500-potassium chloride with the polished electrodes; the conductivity water used throughout had a specific conductivity of 2×10^{-6} mho. A larger cell of the same type (capacity 2 c.c.) was employed in experiments where relatively large quantities of pure material were available. The measurements were carried out at 25°±0·01°, the solutions being made up with water at this temperature; the same apparatus was used throughout, so the results are strictly comparable. From considerations of space, complete lists of the readings are not included, but readings of the variation in conductivity at 5- and 10-minute intervals (unless the reading remained constant) were taken in all cases. κ_1, κ_2, and κ_3 refer respectively to the conductivity (in gemmhos) of an M/2-aqueous solution of the sugar or sugar derivative concerned, of the M/2-boric acid solution employed, and of a solution in M/2-boric acid of the sugar or sugar derivative at the same concentration.

α-d-*Glucose*.—α-*d*-Glucose was prepared according to Hudson and Dale (*J. Amer. Chem. Soc.*, 1917, **39**, 322). The specific conductivity was reduced by grinding with pyridine at room temperature, filtration, and precipitation and washing with alcohol. Solvent was finally removed in a vacuum at 40° : $[\alpha]_D^{20°}$ + 106° in water (*c*, 3·0) (after 2 mins.).

$\kappa_1 = 11{\cdot}5$; $\kappa_2 = 27{\cdot}6$.

Time (mins.) ……	5	30	60	80	100	120
κ_3 ………………	96·3	89·8	86·0	84·7	83·8	83·3 (constant value).

Elevation of conductivity : 59·4 (initial value; by extrapolation); 44·2 (final value).

β-d-*Glucose*.—β-*d*-Glucose, prepared by Behrend's method (*Annalen*, 1907, **353**, 107), was well washed with alcohol to remove pyridine, and the solvent removed as before: $[\alpha]_{\mathrm{D}}^{20^\circ} + 19\cdot5^\circ$ in water (*c*, 1·0) (after 3 mins.).

$\kappa_1 = 8\cdot5$; $\kappa_2 = 28\cdot0$.

Time (mins.)	12	20	30	60	80	100
κ_3	66·6	68·3	70·0	73·1	74·1	75·0 (constant value).

Elevation of conductivity: 26·5 (initial value; by extrptn.); 38·5 (final value).

It will be noted that a difference exists between the final values—expressed as elevations of conductivity—for α- and β-glucose. Böeseken (*loc. cit.*) also found this to be the case. The same "gap" was found to occur if the α- and β-glucose solutions were allowed to come to equilibrium before the addition of boric acid.

α-d-*Galactose*.—Kerfoot's "pure" galactose was found to be almost entirely α-*d*-galactose, and after being washed with 90% ethyl alcohol it gave $[\alpha]_{\mathrm{D}}^{20^\circ} + 137\cdot8^\circ$ in water (*c*, 1·3) (after 3 mins.).

$\kappa_1 = 23\cdot3$; $\kappa_2 = 27\cdot9$.

Time (mins.)	10	40	60	100
κ_3	78·4	74·4	73·1	72·2 (constant value).

Elevation of conductivity: 29·5 (initial; by extrptn.); 21·0 (final).

β-d-*Mannose*.—In aqueous solution six samples of mannose had a high conductivity, not reduced by recrystallisation: $[\alpha]_{\mathrm{D}}^{15^\circ} - 17\cdot0^\circ$ in water (*c*, 3·0) (initial value), $+ 14\cdot8^\circ$ (final value).

$\kappa_1 = 78\cdot2$; $\kappa_2 = 28\cdot0$.

Time (mins.)	7	15	30	50
κ_3	105·8	104·9	104·1	103·8 (constant value).

Elevation of conductivity: 0·4 (initial; by extrptn.); $-$ 2·4 (final).

α-l-*Rhamnose*.—Specimen from B.D.H. of high purity: $[\alpha]_{\mathrm{D}}^{18^\circ} - 6\cdot8^\circ$ in water (*c*, 1·0) (after 3 mins.); $+ 9\cdot0^\circ$ (final value).

$\kappa_1 = 5\cdot2$; $\kappa_2 = 29\cdot0$.

Time (mins.)	5	100
κ_3	41·8	46·1 (constant value).

Elevation of conductivity: 7·5 (initial; by extrptn.); 11·9 (final).

Sucrose.—$[\alpha]_{\mathrm{D}}^{20^\circ} + 66\cdot4^\circ$ in water (*c*, 3·0).

$\kappa_1 = 7\cdot8$; $\kappa_2 = 28\cdot9$; $\kappa_3 = 27\cdot2$. *Depression of conductivity*: 9·5 (constant value).

α-*Methylglucopyranoside*.—This was prepared according to Patterson and Robertson (J., 1929, 300), and after 5 recrystallisations from absolute alcohol had m. p. 167°, $[\alpha]_{\mathrm{D}}^{20^\circ} + 159^\circ$ in water (*c*, 3·0) (Found: OMe, 15·4. Calc. for $C_7H_{14}O_6$: OMe, 16·0%).

$\kappa_1 = 3\cdot9$; $\kappa_2 = 27\cdot9$; $\kappa_3 = 22\cdot5$. *Depression of conductivity*: 9·3.

α-*Methylgalactopyranoside*.—Prepared as above, this had m. p. 116°, $[\alpha]_{\mathrm{D}}^{20^\circ} + 179^\circ$ in water (*c*, 1·0) (Found: OMe, 15·9. Calc. for $C_7H_{14}O_6$: OMe, 16·0%).

$\kappa_1 = 12\cdot9$; $\kappa_2 = 27\cdot9$; $\kappa_3 = 36\cdot8$. *Depression of conductivity*: 4·0.

2 : 3 : 4 : 6-*Tetramethyl Glucose*.—This sugar was prepared by the method of West and Holden (*J. Amer. Chem. Soc.*, 1934, **56**, 930) and recrystallisation from light petroleum gave a product, m. p. 85—88° (Found: OMe, 51·5. Calc. for $C_{10}H_{20}O_6$: OMe, 52·5%); $\kappa_1 = 50$. By 5 distillations at 135° (bath temp.)/0·03 mm., a specimen of the glucopyranose was secured with m. p. 72°, $[\alpha]_{\mathrm{D}}^{20^\circ} + 70\cdot3^\circ$ in water (*c*, 0·5) $\longrightarrow + 79\cdot8^\circ$ (constant value).

$\kappa_1 = 7\cdot0$; $\kappa_2 = 27\cdot9$; $\kappa_3 = 20\cdot8$. *Depression of conductivity*: 14·1.

Tetramethyl Methylglucopyranoside.—West and Holden's method (*loc. cit.*) was employed, and the syrup distilled twice at 85°/0·04 mm. with a fractionating column; $n_{\mathrm{D}}^{18^\circ}$ 1·4465 (Found: OMe, 60·5. Calc. for $C_{11}H_{22}O_6$: OMe, 62·0%).

$\kappa_1 = 12\cdot2$; $\kappa_2 = 27\cdot6$; $\kappa_3 = 21\cdot5$. *Depression of conductivity*: 18·3.

2 : 3 : 6-*Trimethyl Methylglucopyranoside.*—Starch was methylated according to Haworth, Hirst, and Webb (J., 1928, 2681) until the methoxyl content reached 44%. Hydrolysis by the method of Baird, Haworth, and Hirst (J., 1935, 1201) yielded a mixture of tri- and tetramethyl methylglucosides which were fractionated in a high vacuum, the first runnings being rejected. A colourless syrup, $n_{\mathrm{D}}^{18^\circ}$ 1·4550, was obtained (Found : OMe, 51·5. Calc. for $C_{10}H_{20}O_6$: OMe, 52·5%).

$\kappa_1 = 14{\cdot}1$; $\kappa_2 = 27{\cdot}6$; $\kappa_3 = 25{\cdot}5$. *Depression of conductivity :* 16·2.

2 : 3 : 6-*Trimethyl Glucopyranose.*—Hydrolysis of the corresponding methylglucoside by means of aqueous hydrochloric acid, followed by isolation in the usual way, yielded the sugar, after recrystallisation from ether, of m. p. 117° : $[\alpha]_{\mathrm{D}}^{18^\circ} + 66^\circ$ in water (*c*, 1·4) (final value) (Found : OMe, 40·5. Calc. for $C_9H_{18}O_6$: OMe, 41·8%).

$\kappa_1 = 10{\cdot}4$; $\kappa_2 = 27{\cdot}9$; $\kappa_3 = 28{\cdot}8$. *Depression of conductivity :* 9·5.

3 : 4 : 6-*Trimethyl* α-d-*Mannose.*—Bott, Haworth, and Hirst's method (*loc. cit.*) was used. Care was necessary to keep the intermediate "γ"-tetra-acetyl methylmannoside from becoming even faintly acid, the addition of sodium bicarbonate being necessary to prevent this. The product (Found : C, 48·5; H, 8·1; OMe, 41·0. Calc. for $C_9H_{18}O_6$: C, 48·7; H, 8·1; OMe, 41·8%) had m. p. 104°, $[\alpha]_{\mathrm{D}}^{20^\circ} + 22^\circ$ in water (*c*, 0·6) (initial value) falling to + 8·3° (constant value). The same results were obtained in boric acid solution.

$\kappa_1 = 18{\cdot}0$; $\kappa_2 = 27{\cdot}0$.

Time (mins.)	6	15	20	40	60	80
κ_3	34·8	36·4	37·2	39·4	40·3	40·9 (equilibrium value)

Depression of conductivity : 12·1 (initial), 4·1 (final).

Glucose Diethylmercaptal.—The product obtained by Fischer's method (*Ber.*, 1894, **27**, 673) was recrystallised repeatedly from water; m. p. 128°.

$\kappa_1 = 11{\cdot}7$; $\kappa_2 = 5{\cdot}1$; $\kappa_3 = 193{\cdot}0$. *Elevation of conductivity :* 176·2.

Ethylene Glycol.—$\kappa_1 = 4{\cdot}8$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 27{\cdot}1$. *Depression of conductivity :* 7·7.

Glycerol.—$\kappa_1 = 7{\cdot}2$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 45{\cdot}3$. *Elevation of conductivity :* 8·1.

αβ-*Propylene Glycol.*—$\kappa_1 = 16{\cdot}2$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 33{\cdot}5$. *Depression of conductivity :* 12·7.

Triethylene Glycol.—$\kappa_1 = 7{\cdot}6$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 23{\cdot}1$. *Depression of conductivity :* 14·5.

Erythritol.—$\kappa_1 = 25{\cdot}0$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 97{\cdot}0$. *Elevation of conductivity :* 42·0.

Dulcitol.—$\kappa_1 = 35{\cdot}9$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 660$. *Elevation of conductivity :* 594.

Mannitol.—$\kappa_1 = 12{\cdot}3$; $\kappa_2 = 29{\cdot}0$; $\kappa_3 = 667{\cdot}3$. *Elevation of conductivity :* 626.

γ-*Methylglucoside.*—Fischer's method (*Ber.*, 1914, **47**, 1984) was employed, and the product when distilled at 220° (bath temp.)/0·04 mm. had no action on Fehling's solution; $[\alpha]_{\mathrm{D}}^{18^\circ} - 14^\circ$ in water (*c*, 5·0) (Found : OMe, 15·8. Calc. for $C_7H_{14}O_6$: OMe, 16·0%).

$\kappa_1 = 15{\cdot}0$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 156{\cdot}3$. *Elevation of conductivity :* 111·3.

γ-*Methylgalactoside.*—The method of Haworth, Ruell, and Westgarth (J., 1924, **125**, 2468) gave a non-reducing syrup, $[\alpha]_{\mathrm{D}}^{18^\circ} - 57{\cdot}6^\circ$ in water (*c*, 2·3) (Found : OMe, 15·1%). Comparison of the rate of hydrolysis in N/10-hydrochloric acid at 90° with that for α-methylgalactopyranoside showed that, whereas only 50% of the latter was hydrolysed during 9 hours, the furanoside was completely hydrolysed in 5 hours.

$\kappa_1 = 30{\cdot}0$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 48{\cdot}0$. *Depression of conductivity :* 12·0.

α-*Methylmannofuranoside.*—Haworth, Hirst, and Webb's method (J., 1930, 658) yielded a colourless, non-reducing syrup which crystallised immediately on nucleation with a crystal of the substance kindly provided by Professor Haworth; m. p. 119°; $[\alpha]_{\mathrm{D}}^{18^\circ} + 113^\circ$ in water (*c*, 1·5), + 112·2° in M/2-boric acid (*c*, 0·5).

$\kappa_1 = 20{\cdot}0$; $\kappa_2 = 30{\cdot}0$; $\kappa_3 = 3400$. *Elevation of conductivity :* 3350.

β-d-*Fructose.*—Commercial fructose was purified by slow recrystallisation from absolute alcohol and washing with acetone; $[\alpha]_D^{17°}$ − 130° in water (c, 3·6).

$\kappa_1 = 28·6$; $\kappa_2 = 30·0$; $\kappa_3 = 762$. *Elevation of conductivity :* 703.

α-l-*Sorbose.*—M. p. 164—165°, $[\alpha]_D^{18°}$ − 43·5° in water (c, 1·0).

(i) $\kappa_1 = 24·8$; $\kappa_2 = 30·0$; $\kappa_3 = 2214$. *Elevation of conductivity :* 2159.

(ii) For M/10-solutions in each case : $\kappa_1 = 9·3$; $\kappa_2 = 5·1$; $\kappa_3 = 212$. *Elevation of conductivity :* 197·6.

Rotation Experiments.

α-d-*Glucose.*—The values of $[\alpha]_D^{20°}$ at time t (mins.) for (i) M/2-aqueous solution and (ii) M/2-solution in M/2-boric acid were :

t	5	30	60	140	220	280	∞
$[\alpha]_D^{20°}$ (i)	+108·2°	94·1°	82·6°	64·4°	57·6°	54·9°	52·7°
$[\alpha]_D^{20°}$ (ii)	+108·3°	94·0°	82·8°	64·8°	57·4°	54·7°	52·6°

Similar experiments were carried out with M/4- and M/8-solutions; the figures in each case showed the same rate of mutarotation in aqueous and boric acid solution and the equilibrium values only varied from 52·3° to 52·6°.

β-d-*Glucose.*—The data, expressed as above, are :

t	3	20	40	60	90	150	240	∞
$[\alpha]_D^{20°}$ (i)	+20·6°	25·7°	30·6°	34·6°	39·2°	44·7°	49·0°	52·2°
$[\alpha]_D^{20°}$ (ii)	+20·8°	25·8°	30·8°	34·8°	39·2°	44·7°	49·2°	52·3°

Viscosity Experiments.

The apparatus used was that described by Hornel and Butler (J., 1936, 1361); it required less than 1 c.c. of liquid for a determination, and the capillary was of such dimensions that approximately 100 seconds were required for water to pass between the fixed points. M/2-Solutions of the substances examined were made up in water and in boric acid solution; a weighed amount of solution was transferred to the apparatus, and its time of flow determined by means of a Venner stop-watch reading to 0·1 sec., the mean of several determinations at 25° ± 0·02° being taken as the result.

The relative viscosity η_r was calculated from $\eta_r = \eta'/\eta = \rho'T'/\rho T$, where η and η' are the viscosity coefficients of two liquids of densities ρ and ρ' and times of fall T and T'. The results are recorded in the following table, in which G denotes the weight (in g.) in the viscometer, and T the mean time of fall (in secs.).

Relative Viscosities.

	M/2-*Aqueous solutions.*			M/2-*Solutions in* M/2-*boric acid.*		
	G.	T.	η_r.	G.	T.	η_r.
(Conductivity water)	0·9445	102·5	1·000	—	—	—
α-*d*-Glucose	0·971	124·2	1·250	0·982	128·9	1·240
β-*d*-Glucose	0·973	124·3	1·250	0·983	129·4	1·245
α-Methylglucopyranoside	0·967	129·7	1·295	0·978	134·2	1·290
3 : 4 : 6-Trimethyl α-mannose	0·967	136·5	1·360	0·977	141·1	1·350
2 : 3 : 6-Trimethyl methylglucopyranoside	0·962	140·7	1·400	0·972	146·0	1·400
2 : 3 : 4 : 6-Tetramethyl glucose	0·962	139·5	1·390	0·973	145·4	1·390
2 : 3 : 4 : 6-Tetramethyl methylglucoside	0·966	142·2	1·420	0·976	148·0	1·415
Boric acid	0·959	106·4	1·050	—	—	—

As shown by the following table, Einstein's equation (*loc. cit.*), which can be modified to $\eta_{sp.}S/c = K$, is approximately obeyed, K having a mean value of 0·44 for the solutions in M/2-boric acid. Here $\eta_{sp.}$ is the specific viscosity, c the weight concentration of dissolved phase, S the density of dissolved phase calculated from a knowledge of the weight of substance taken, the volume of water used, and the weight of solution, and K should be constant for any one class of substance.

It will be noted that the relative viscosity increases with increase in molecular weight; this is analogous to the increasing depression of conductivity on the introduction of an increasing number of methoxyl groups, and both these results are complementary to the above relation between viscosity and molecular volume.

Comparison of Viscosity with Volume of Dissolved Phase for M/2-*Aqueous Solutions.*

Dissolved phase.	$\eta_{sp.}$	*c.*	$\eta_{sp.}/c$.	*S.*	$\eta_{sp.}S/c$.
α-*d*-Glucose	0·250	8·25	0·0303	1·552	0·46
β-*d*-Glucose	0·250	8·25	0·0303	1·552	0·46
α-Methylglucopyranoside	0·295	8·82	0·0335	1·386	0·48
3 : 4 : 6-Trimethyl α-mannose	0·360	9·98	0·0361	1·337	0·48
2 : 3 : 6-Trimethyl methylglucopyranoside	0·400	10·55	0·0379	1·242	0·47
2 : 3 : 4 : 6-Tetramethyl glucose	0·390	10·55	0·0370	1·242	0·46
2 : 3 : 4 : 6-Tetramethyl methylglucoside	0·420	11·10	0·0378	1·275	0·48

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