526. *Aspects of Stereochemistry. Part XVIII.*[1] *Acidic Hydrolysis of* 1,2:5,6-*Di*-O-*isopropylidene*-D-*mannitol* 3,4-*Cyclic Sulphate and* 1,3:2,4-*Di*-O-*ethylidene*-D-*glucitol* 5,6-*Cyclic Sulphate.*

By J. S. Brimacombe, M. E. Evans, A. B. Foster, and J. M. Webber.

The preparation of 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-cyclic sulphate and 1,3:2,4-di-*O*-ethylidene-D-glucitol 5,6-cyclic sulphate is described. Hot, dilute acid converts the former into 1,4-anhydro-D-talitol (88%) and D-mannitol, and the latter into 3,6-anhydro-D-glucitol (72%) and D-glucitol. The mechanism of these reactions is discussed.

In an earlier Paper[2] the acidic hydrolysis of cyclic sulphates derived from various aliphatic and alicyclic vicinal diols was described. We now report an extension of this work to certain carbohydrate cyclic sulphates.

1,2:5,6-Di-*O*-isopropylidene-D-mannitol was converted into the 3,4-cyclic sulphite by reaction with thionyl chloride in pyridine,[3] and thence into the 3,4-cyclic sulphate (I) by oxidation with calcium permanganate in wet acetic acid.[4] Similarly, 1,3:2,4-di-*O*-ethylidene-D-glucitol was converted into the 5,6-cyclic sulphate (VIII) and 3,4-*O*-isopropylidene-D-mannitol into the 1,2:5,6-di(cyclic sulphate); the sulphates and intermediate sulphites were crystalline solids of moderate stability.

Previous attempts[2] to obtain methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-cyclic sulphate by the above method failed, presumably because oxidation of the cyclic sulphite was accompanied by hydrolysis. The cyclic sulphates (I) and (VIII) were obtained in only *ca.* 20% yield and the 3,4-*O*-isopropylidene-D-mannitol 1,2:5,6-di(cyclic sulphate) in 3% yield. Jennings and Jones[5] prepared the glucoside cyclic sulphate by reaction of the parent diol with sulphuryl chloride and treatment of the resultant dichlorosulphate with pyridine. 1,2:5,6-Di-*O*-isopropylidene-D-mannitol 3,4-cyclic sulphate was also made[5] by this method but the physical constants (m. p. 114—118°, $[\alpha]_D$ +41° in $CHCl_3$) were significantly different from those (m. p. 127°, $[\alpha]_D$ +28·5° in $CHCl_3$) of compound (I). However, repetition of Jennings and Jones's procedure gave a product identical with compound (I).

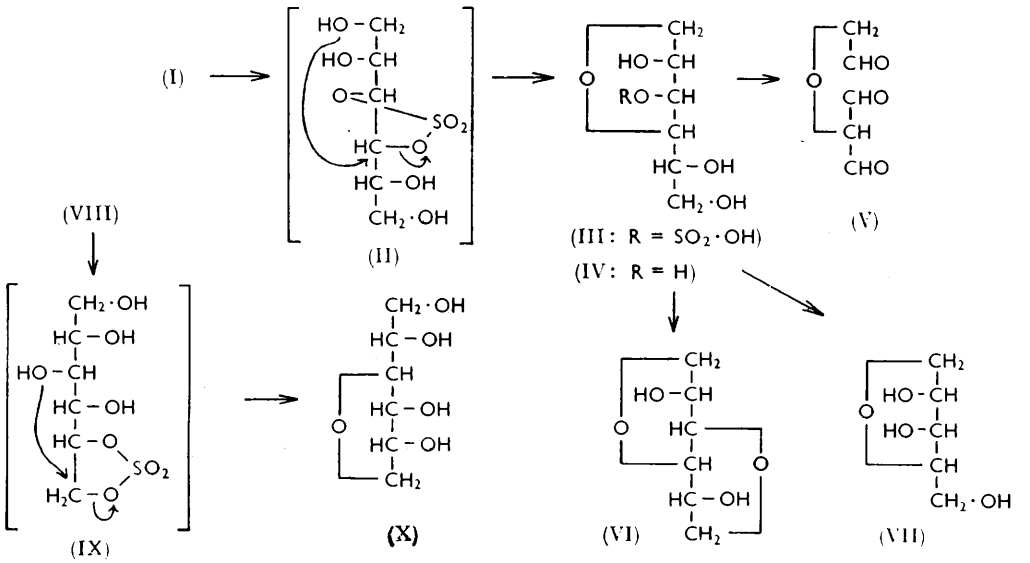
When 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-cyclic sulphate was treated with 0·034N-sulphuric acid at 95—100°, one equivalent of acid was released within 15 minutes and the second equivalent during 6 hours. Examination of the hydrolysate by paper chromatography revealed the progressive formation of a hexitol and an anhydrohexitol, and the concomitant disappearance of an unidentified component of high R_F value. Fractionation of the hydrolysate on cellulose powder gave the hexitol which, on acetylation, afforded D-mannitol hexa-acetate; no evidence was obtained for the presence of other hexitols. The chromatographically homogeneous anhydrohexitol failed to crystallise but was characterised as its di-*O*-isopropylidene derivative and subsequently identified as 1,4-anhydro-D-talitol (3,6-anhydro-D-altritol) (IV). Fractionation of the hydrolysate on Dowex 1 × 2 (OH^- form) according to the procedure of Buchanan and his co-workers[6] revealed it to contain at least 88% of 1,4-anhydro-D-talitol.

The structure of 1,4-anhydro-D-talitol (IV) was assigned on the following evidence. The compound reacted relatively rapidly with 2 mol. of periodate, and the product subsequently underwent a slow overoxidation reaction. Such a pattern would be expected for a molecule containing a vicinal *cis*-diol attached to a five-membered ring and an acylic

[1] Part XVII, Bukhari, Foster, and Webber, *J.*, 1964, 2514.
[2] Brimacombe, Foster, Hancock, Overend, and Stacey, *J.*, 1960, 201.
[3] Carlson and Cretcher, *J. Amer. Chem. Soc.*, 1947, **69**, 1952.
[4] Garner and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5497.
[5] Jennings and Jones, *Canad. J. Chem.*, 1963, **41**, 1151.
[6] Austin, Hardy, Buchanan, and Baddiley, *J.*, 1963, 5350.

vicinal diol since both units would react rapidly with periodate. A close analogy is provided [7] by D-mannono-γ-lactone, the two vicinal diol groups of which are attacked at the same rate by periodate; further comparable results have been obtained by Ferrier.[8] The slow overoxidation is typical [9] of malondialdehyde derivatives, such as structure (V), which would arise from 1,4-anhydro-D-talitol by glycol cleavage.

The structural features present in 1,4-anhydro-D-talitol (IV) are also present in 3,6-anhydro-D-mannitol,[10] and a close parallel was observed in the properties of the respective di-*O*-isopropylidene derivatives. With 70% acetic acid at 30—35°, 1,4-anhydro-2,3:5,6-di-*O*-isopropylidene-D-talitol gave a mono-*O*-isopropylidene derivative which, on reaction in sequence with sodium periodate, sodium borohydride, and dilute acid, gave a 1,4-anhydropentitol (VII) to which the L-*ribo*-configuration was assigned by comparison of its physical properties with those of 1,4-anhydro-DL- and -D-ribitol (see Experimental section). The mono-*O*-isopropylidene derivative was, therefore, 1,4-anhydro-2,3-*O*-isopropylidene-D-talitol or -L-allitol. Whilst the formation of 1,4-anhydro-D-talitol in the acidic hydrolysis of 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-cyclic sulphate may be readily explained (see below), no reasonable mechanism can be presented for the formation of 1,4-anhydro-



L-allitol. Additionally, it has been shown by direct comparison that the 1,4-anhydro-2,3:5,6-di-*O*-isopropylidene-D-talitol described above is identical with the product obtained by reduction and subsequent isopropylidenation of 3,6-anhydro-D-altrose.[11]

That the formation of the 1,4-anhydro-ring during the acid treatment of compound (I) occurred simultaneously with the cleavage of the cyclic sulphate to give 1,4-anhydro-D-talitol 3-(hydrogen sulphate) (III) was established as follows. 1,2:5,6-Di-*O*-isopropylidene-D-mannitol 3,4-cyclic sulphate was treated with acid until approximately one equivalent of acid was released, and the product then subjected in sequence to periodate oxidation, borohydride reduction, and acidic hydrolysis. The major product was 1,4-anhydro-L-ribitol (VII); the presence of the 3-(hydrogen sulphate) group in compound (III) would prevent attack by periodate at the 2,3-position. Further evidence for the formation of

[7] Woods and Neish, *Canad. J. Chem.*, 1954, **32**, 404.
[8] Ferrier, *J.*, 1962, 3544.
[9] Cantley, Hough, and Pittet, *J.*, 1963, 2527, and references therein; Bose, Foster, and Stephens, *J.*, 1959, 3314.
[10] Foster and Overend, *J.*, 1951, 680.
[11] Dr. J. G. Buchanan, personal communication.

compound (III) was provided by the formation of 1,4:3,6-dianhydro-D-iditol (VI), characterised as the 2,5-di-*O*-benzoate, when the product formed after the release of one equivalent of acid from compound (I) in the acidic hydrolysis was treated with base.

The behaviour of 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-cyclic sulphate in acid hydrolysis parallels that observed [12,13] for the cyclic sulphate of ethane-1,2-diol * in that rapid cleavage occurs to give the half-ester which is subsequently hydrolysed relatively slowly, with S–O bond cleavage, to the diol. Westheimer and his co-workers [12] showed that, in the pH range 2—10, the first stage of the hydrolysis is a first-order solvolysis, occurring mainly with C–O bond cleavage. Such a cleavage is clearly the main course of reaction with 1,2:5,6-di-*O*-isopropylidene-D-manntiol 3,4-cyclic sulphate where the incoming nucleophile is a terminal oxygen function in the same molecule. The course of the reaction is probably not significantly influenced by the isopropylidene groups since they would be cleaved very rapidly [14] in the acid hydrolysis. The origin of the small amount of D-mannitol in the hydrolysate is not clear. It could have resulted from C–O bond cleavage with retention of configuration, with a water molecule as the incoming nucleophile, or by limited S–O bond cleavage in the opening of the cyclic sulphate.

When 1,3:2,4-di-*O*-ethylidene-D-glucitol 5,6-cyclic sulphate (VIII) was treated with hot dilute acid, as for the D-mannitol derivative (I), approximately one equivalent of acid was released in 15 minutes and 1·86 equivalents after 8 hours. Fractionation of the hydrolysis products on Amberlite IRA 400 (OH^- form) gave *ca.* 72% of 3,6-anhydro-D-glucitol and *ca.* 17% of D-glucitol (characterised as the hexa-acetate). Additionally, traces of a component were detected with chromatographic properties similar to those of 2,5-anhydro-D-iditol.[15]

The 3,6-anhydro-D-glucitol (X) clearly originates by C(6)–O bond cleavage in the cyclic sulphate (IX) with O-3 as the intramolecular nucleophile. Since the cyclic acetal groups in compound (VIII) would be rapidly cleaved in the acid hydrolysis [14] they probably exert little influence on the course of the reaction. Three origins for the D-glucitol are possible; S–O bond cleavage in the opening of the cyclic sulphate, C(6)–O bond cleavage with a water molecule as the nucleophile, or C(5)–O bond cleavage with retention of configuration, with a water molecule as the nucleophile. The reason for the formation of little, if any, 2,5-anhydro-D-iditol may be steric in origin. If the preferred conformation of compound (IX) involves a planar zig-zag of the carbon chain then only a small distortion will be necessary in order to bring O-3 into a position to attack C-6 as C(6)–O bond cleavage occurs, whereas very extensive deformation to an unfavourable conformation is involved in bringing O-2 into a position to attack C-5 as C(5)–O bond cleavage occurs. Alternatively, the 5,6-cyclic sulphate group may undergo solvolysis at the primary position, *i.e.*, with preferential cleavage of the C(6)–O bond.

Experimental

Paper chromatography was performed on Whatman No. 1 paper by downward irrigation with butanol–ethanol–water (4 : 1 : 5), and detection with silver nitrate.[16] Light petroleum had b. p. 60—80°.

Preparation of Cyclic Sulphites.—A mixture of thionyl chloride (15 ml.) and dichloromethane (50 ml.) was added during 2 hr. to a cooled (0°), stirred solution of 1,2:5,6-di-*O*-isopropylidene-D-mannitol [17] (50 g.) in dichloromethane (350 ml.) and pyridine (40 ml.). After removal of the

* In a preceding Paper [2] there is an error in the legend to Fig. 3. Curve *C* shows the development of acidity on acid treatment of the cyclic sulphate of cyclohexane-*trans*-1,2-diol and not of ethylene sulphate as indicated.

[12] Kaiser, Panar, and Westheimer, *J. Amer. Chem. Soc.*, 1963, **85**, 602.
[13] Brimacombe, Ph.D. Thesis, Birmingham, 1959.
[14] Barker and Bourne, *Adv. Carbohydrate Chem.*, 1952, **7**, 138.
[15] Dekker and Hashizume, *Arch. Biochem. Biophys.*, 1958, **78**, 348.
[16] Trevelyan, Proctor, and Harrison, *Nature*, 1950, **166**, 444.
[17] Baer, Grosheintz, and Fischer, *J. Amer. Chem. Soc.*, 1939, **61**, 2607.

pyridine hydrochloride, the filtrate was washed successively with ice-cold, aqueous potassium carbonate, ice-cold 0·1N-hydrochloric acid (3 × 1 l.), and water (3 × 1 l.). The dried ($MgSO_4$) organic layer was evaporated and the residue was recrystallised from ethanol–light petroleum, to give 1,2:5,6-*di*-O-*isopropylidene*-D-*mannitol* 3,4-*cyclic sulphite* (44 g., 71%), m. p. 82—83°, $[\alpha]_D$ +93° (*c* 5·1 in $CHCl_3$) (Found: C, 46·7; H, 6·7; S, 10·3. $C_{12}H_{20}O_7S$ requires C, 46·7; H, 6·5; S, 10·4%).

Similarly prepared were 1,3:2,4-*di*-O-*ethylidene*-D-*glucitol* 5,6-*cyclic sulphite* (50%), m. p. 117—118°, $[\alpha]_D$ −45° (*c* 1·5 in $CHCl_3$) (Found: C, 42·9; H, 5·7; S, 11·3. $C_{10}H_{16}O_7S$ requires C, 42·9; H, 5·7; S, 11·4%), and 3,4-O-*isopropylidene*-D-*mannitol* 1,2:5,6-*di*(*cyclic sulphite*) (50%), m. p. 103—104°, $[\alpha]_D$ −47° (*c* 1·6 in $CHCl_3$) (Found: C, 34·7; H, 4·3; S, 20·2. $C_9H_{14}O_8S_2$ requires C, 34·4; H, 4·5; S, 20·4%).

Preparation of Cyclic Sulphates.—A filtered solution of calcium permanganate (10 g.) in water (15 ml.) was added to a stirred, cooled solution of 1,2:5,6-di-*O*-isopropylidene-D-mannitol 3,4-cyclic sulphite (7·7 g.) in glacial acetic acid (100 ml.); the temperature of the mixture was kept below 15°. Ice and ice-cold saturated aqueous sodium hydrogen sulphite were added to dissolve the manganese dioxide, and the mixture was extracted with an equal volume of chloroform. The extract was washed with aqueous potassium carbonate, until free from acetic acid, and then with water. Concentration of the dried ($MgSO_4$) extract and recrystallisation of the residue from ethanol–light petroleum gave 1,2:5,6-di-O-*isopropylidene*-D-*mannitol* 3,4-*cyclic sulphate* (1·7 g., 21%), m. p. 127° (decomp.), $[\alpha]_D$ +28·5° (*c* 3·7 in $CHCl_3$) (Found: C, 44·8; H, 6·2; S, 10·0. $C_{12}H_{20}O_8S$ requires C, 44·5; H, 6·2; S, 9·9%).

Similarly prepared were 1,3:2,4-*di*-O-*ethylidene*-D-*glucitol* 5,6-*cyclic sulphate* (17%), m. p. 119—121° (decomp.), $[\alpha]_D$ −8° (*c* 0·8 in $CHCl_3$) (Found: C, 40·7; H, 5·4; S, 10·9. $C_{10}H_{16}O_8S$ requires C, 40·6; H, 5·4; S, 10·8%), and 3,4-O-*isopropylidene*-D-*mannitol* 1,2:5,6-*di*(*cyclic sulphate*) (3%), m. p. 110—116° (decomp.), $[\alpha]_D$ −15° (*c* 0·95 in $CHCl_3$) (Found: C, 31·15; H, 3·9. $C_9H_{14}O_{10}S_2$ requires C, 31·2; H, 4·1%).

Acidic Hydrolysis of 1,2:5,6-*Di*-O-*isopropylidene*-D-*mannitol* 3,4-*Cyclic Sulphate.*—(*a*) The cyclic sulphate (0·97 g.) was added to 0·034N-sulphuric acid (25 ml.) at 95—100° and, at suitable intervals, aliquots (2 ml.) were withdrawn, rapidly cooled to 0°, and titrated with 0·1N-sodium hydroxide to Methyl Red. The following results were obtained:

Time (min.)	15	50	100	180	300	365	420
Acid released (equiv.)	1·02	1·17	1·36	1·59	1·82	2·00	2·09

In a parallel experiment, aliquot portions were neutralised with methyldi-n-octylamine [18] and examined by paper chromatography. Components with R_F 0·25 (mannitol) and 0·34 (1,4-anhydro-D-talitol) were observed to increase in amount with the duration of the hydrolysis, whilst the amount of a component with R_F 0·7 (unidentified) decreased progressively.

(*b*) A mixture of the cyclic sulphate (2·4 g.) and 0·03N-sulphuric acid (75 ml.) was maintained at 95—100° for 6 hr., cooled, and neutralised with methyldi-n-octylamine. Concentration of the aqueous solution and fractionation of the residue (1·3 g.) on a column (5 × 70 cm.) of cellulose powder (W. and R. Balston Ltd., standard grade), using the same solvent system as for paper chromatography and collecting 25 ml. fractions, gave the following results: fractions 70—80 gave the component (*ca.* 5 mg.) with R_F 0·7; fractions 96—115 gave the component with R_F 0·34, subsequently identified as 1,4-anhydro-D-talitol; fractions 125—136 gave a product with R_F 0·24, which, on treatment with acetic anhydride and sodium acetate in the usual way, gave D-mannitol hexa-acetate, m. p. (from ethanol) and mixed m. p. 124°. The components from these groups of fractions were chromatographically homogeneous.

(*c*) A hydrolysis product (0·177 g.) obtained as in (*b*) above was introduced on to a column (3·5 × 45 cm.) of Dowex 1 × 2 resin (OH^- form) prepared as described by Austin *et al.*[6] On washing with water (25 ml. fractions) a small amount of D-mannitol was eluted (fractions 10—19), followed by chromatographically homogeneous 1,4-anhydro-D-talitol (0·156 g., fractions 20—25). Subsequent fractions contained a further, small amount of the anhydro-compound but no other components could be detected.

Identification of 1,4-*Anhydro*-D-*talitol.*—A mixture of the anhydro-compound (0·96 g.), acetone (30 ml.), and concentrated sulphuric acid (0·52 ml.) was stirred overnight and neutralised with potassium carbonate. The filtered solution was evaporated, and a solution of the residue in chloroform (100 ml.) was washed with water and evaporated. Distillation of the

[18] Lester Smith and Page, *J. Soc. Chem. Ind.*, 1948, **67**, 48.

residue gave 1,4-*anhydro*-2,3:5,6-*di*-O-*isopropylidene*-D-*talitol* (0·635 g., 45%), b. p. 72—76° (bath)/0·1 mm., $[\alpha]_D$ −37° (*c* 0·9 in $CHCl_3$) (Found: C, 58·5; H, 8·2. $C_{12}H_{20}O_5$ requires C, 59·0; H, 8·2%). The compound crystallised on storage, m. p. 51° (from light petroleum).

A solution of the foregoing di-isopropylidene derivative (0·5 g.) in 70% acetic acid (100 ml.) was kept at 30—35° for 1·5 hr. and then evaporated at 20—25°/12 mm. A solution of the residue in aqueous sodium hydrogen carbonate was extracted with chloroform (30 ml.) and evaporated. The residue was extracted with boiling acetone (7 × 50 ml.) and the combined extracts were concentrated. Distillation of the residue gave 1,4-*anhydro*-2,3-O-*isopropylidene*-D-*talitol* (0·21 g., 50%), b. p. 110—125° (bath)/0·1—0·2 mm., which solidified on storage, m. p. 77—79° (from carbon tetrachloride), $[\alpha]_D$ −43° (*c* 0·8 in $CHCl_3$) (Found: C, 53·0; H, 8·0. $C_9H_{16}O_5$ requires C, 52·9; H, 7·8%).

A solution of the foregoing monoisopropylidene compound (1·2 g.) in water (25 ml.) was treated with a solution of sodium metaperiodate (1·4 g.) in water (25 ml.). After 30 min. at room temperature, sodium borohydride (0·35 g.) was added and the mixture stored overnight. The solution was extracted continuously with chloroform during 30 hr. and the dried ($MgSO_4$) extract was evaporated. The syrupy residue was treated with boiling N-hydrochloric acid (10 ml.) for 4 hr. and the acid was then removed at 100°/~12 mm. Recrystallisation of the residue from methanol gave 1,4-*anhydro*-L-*ribitol* (0·48 g., 61%), m. p. 102—103°, $[\alpha]_D$ −66° (*c* 0·65 in H_2O) (Found: C, 44·6; H, 7·6. $C_5H_{10}O_4$ requires C, 44·8; H, 7·5%). The compound had the same R_F value on paper chromatography as 1,4-anhydro-DL-ribitol; Kuhn and Wendt [19] record m. p. 99° and $[\alpha]_D$ +66·7° in H_2O, and Weygand and Wirth [20] report m. p. 99° and $[\alpha]_D$ +71° for 1,4-anhydro-D-ribitol.

At intervals, a solution of 1,4-anhydro-D-talitol (91 mg.) in 0·01N-sodium metaperiodate (25 ml.) was analysed for residual periodate by the method of Neümuller and Vasseur.[21] The results were as follows:

Time (min.)	10	30	70	250	495	610	750
Periodate consumed (mol.)	1·41	1·70	2·18	2·28	2·31	2·44	2·76

Graded Acidic Hydrolysis of 1,2:5,6-*Di*-O-*isopropylidene*-D-*mannitol* 3,4-*Cyclic Sulphate*.—A mixture of the cyclic sulphate (1·6 g.) and 0·03N-sulphuric acid (75 ml.) was heated until dissolution occurred. To the cooled solution were added phosphate buffer [22] (50 ml., pH 6·98) and sodium metaperiodate (1·27 g.), and, after 2·5 hr., sodium borohydride (0·5 g.). After 12 hr., the pH of the mixture was adjusted to 1·0 by the addition of concentrated hydrochloric acid, and the solution was boiled under reflux for 12 hr. Iodine was removed by continuous extraction with chloroform, and the aqueous solution was deionised with Amberlite IR 120 (H^+ form) and IRA 400 (OH^- form) and concentrated, to yield 1,4-anhydro-L-ribitol (0·14 g.), m. p. 101—103° (from ethanol), alone or in admixture with the product described above, $[\alpha]_D$ −64° (*c* 0·7 in H_2O).

In a parallel experiment, the cyclic sulphate (3·5 g.) and 0·03N-sulphuric acid (100 ml.) were heated at 95—100° until dissolution occurred (*ca.* 15 min.). N-Sodium hydroxide (100 ml.) was added and the temperature was kept at 95—100° for 2 days. The cooled solution was neutralised with dilute sulphuric acid and evaporated, and the residue was continuously extracted with ethyl acetate for 2 days. Concentration of the extract and benzoylation of the residue in the usual way gave 1,4:3,6-dianhydro-2,5-di-*O*-benzoyl-D-iditol (50 mg.), m. p. 110—111° (from ethanol), alone or in admixture with the authentic compound,[23] $[\alpha]_D$ +131° (*c* 0·9 in $CHCl_3$).

Acidic Hydrolysis of 1,3:2,4-*Di*-O-*ethylidene*-D-*glucitol* 5,6-*Cyclic Sulphate*.—(*a*) When carried out under essentially the same conditions as for the D-mannitol derivative in (*a*) above, the results were as follows:

Time (min.)	20	45	80	160	300	480
Acid released (equiv.)	0·98	1·12	1·25	1·52	1·78	1·86

(*b*) The cyclic sulphate (1·0 g.) was treated with boiling 0·03N-sulphuric acid (25 ml.) for 8 hr. and the pH of the cooled hydrolysate was adjusted to 7 with aqueous barium hydroxide.

[19] Kuhn and Wendt, *Chem. Ber.*, 1948, **81**, 553.
[20] Weygand and Wirth, *Chem. Ber.*, 1952, **85**, 1000.
[21] Neümuller and Vasseur, *Arkiv Kemi Mineral Geol.*, 1935, **5**, 235.
[22] Vogel, "Quantitative Inorganic Analysis," Longmans, London, 1944, p. 809.
[23] Wiggins, *J.*, 1947, 1403.

The filtered solution was evaporated at 100°/12 mm., and a portion (0·143 g.) of the residue (0·6 g.) was fractionated on a column (3·5 × 31 cm.) of Amberlite IRA 400 [200—400 mesh, OH^- form prepared from the Cl^- form by washing with N-sodium hydroxide (1 l.) then with deionised water (cf. Austin *et al.*[6])]. Elution was effected with water, and 10 ml. fractions were collected. Paper chromatography revealed D-glucitol in fractions 70—85, whilst fractions 70—150 gave a product (24 mg.) which was shown by paper chromatography to contain mainly D-glucitol, together with a trace of a compound with an R_F value similar to that of 2,5-anhydro-D-iditol (prepared by the method of Dekker and Hashizume [15]). Acetylation of the product from fractions 70—150 with acetic anhydride and sodium acetate gave D-glucitol hexa-acetate, m. p. and mixed m. p. 100°, $[\alpha]_{5461}$ +12° (*c* 4·2 in $CHCl_3$). Fractions 151—220 gave 3,6-anhydro-D-glucitol (0·103 g.), m. p. (from ethanol) and mixed m. p.[24] 112—116°, $[\alpha]_{5461}$ −7·5° (*c* 1·7 in H_2O); the authentic compound had $[\alpha]_{5461}$ −6° in water.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY,
BIRMINGHAM 15.

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[24] Montgomery and Wiggins, *J.*, 1946, 390.