Products from the Alkaline and Reductive Fission of the Epoxide Ring of Methyl 3 : 4- *and* 2 : 3-*Anhydro*-6-*deoxy*-α-L-*taloside and of their Methylated Derivatives.*

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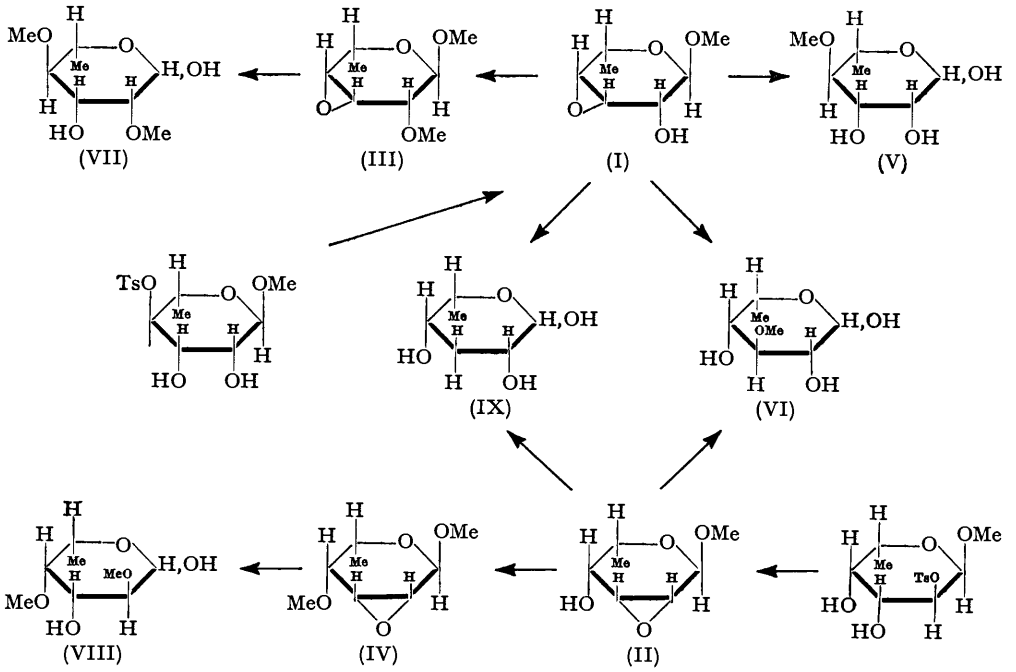
6-Deoxy-3-*O*-methyl-L-idose and 6-deoxy-4-*O*-methyl-L-mannose have been isolated from the alkaline fission of methyl 3 : 4-anhydro-6-deoxy-α-L-taloside. Methylation of the hydroxyl group at position 2, before fission, led to the isolation of 6-deoxy-2 : 4-di-*O*-methyl-L-mannose. Similar treatment of the 2 : 3-anhydro-derivatives gave rise to 6-deoxy-3-*O*-methyl-L-idose and 6-deoxy-2 : 4-di-*O*-methyl-L-galactose. Reduction of these epoxide ring compounds with lithium aluminium hydride afforded dideoxy-sugars.

Percival and Zobrist (*J.*, 1953, 564) examined the products of alkaline fission of methyl 2 : 3-anhydro-α-D-lyxoside and found that 2-*O*-methyl-D-xylose and 3-*O*-methyl-D-arabinose were obtained in the ratio of 1 : 2. However, if position 5 was substituted by a methoxyl radical then the only product isolated was 3 : 5-di-*O*-methyl-D-arabinose. These studies have now been extended to methyl 3 : 4- and 2 : 3-anhydro-6-deoxy-α-L-taloside and their methylated derivatives. Alkaline fission of the epoxide ring in methyl 3 : 4-anhydro-6-

deoxy-α-L-taloside (I) led to the isolation of 6-deoxy-4-*O*-methyl-L-mannose (4-*O*-methyl-L-rhamnose) (V) and 6-deoxy-3-*O*-methyl-L-idose (VI) in the ratio of approximately 1 : 2. The isolation of both possible fission products from the 3 : 4-anhydro-derivatives is in direct conformity with the results of Peat and Wiggins (*J.*, 1938, 1088), and of Percival and Zobrist (*loc. cit.*). On the other hand the 2 : 3-anhydro-derivative (II) gave only 6-deoxy-3-*O*-methyl-L-idose (VI) (70—80%) and 6-deoxy-L-idose (10—15%), there being no evidence for the presence of the other isomer, 6-deoxy-2-*O*-methyl-L-galactose (2-*O*-methyl-L-fucose), in the fission products. It is difficult to understand why only the deoxyidose derivative could be found, but steric factors may hinder the formation of the galactose derivative, as Gyr and Reichstein (*Helv. Chim. Acta*, 1945, **28**, 226) record the isolation of only the 3-*O*-methyl-D-idose derivative from methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-α-D-taloside, and Sorkin and Reichstein (*ibid.*, p. 1) the 2-*O*-methyl-D-idose derivative from methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-α-D-guloside.



6-Deoxy-3-*O*-methyl-L-idose has not been described previously and two identical fractions (1*a* and 1*b*), obtained respectively from the sodium methoxide fission of the epoxide ring of the 3 : 4- and the 2 : 3-anhydro-derivatives of talose, may presumably have this constitution as it is the only possible mono-*O*-methyl derivative which can be obtained by this means from both derivatives. Fischer, Bollinger, and Reichstein (*ibid.*, 1954, **37**, 6) have reported, since this work was completed, the synthesis of 6-deoxy-3-*O*-methyl-D-idose and its osazone. The constants recorded for these derivatives are the same (rotations of opposite sign) as those reported by us for the corresponding derivatives of the L-sugar.

From the methylated 3 : 4-anhydro- (III) and 2 : 3-anhydro- (IV) derivatives of talose only a single product was isolated: 6-deoxy-2 : 4-di-*O*-methyl-L-mannose (VII) from the former and 6-deoxy-2 : 4-di-*O*-methyl-L-galactose (VIII) from the latter. Butler, Lloyd, and Stacey (*Chem. and Ind.*, 1954, 107) have reported the synthesis of 6-deoxy-2 : 4-di-*O*-methyl-L-mannose by a different route, and our proof of the constitution of (VII) is based partly on the aniline derivative which is identical with the 6-deoxy-2 : 4-di-*O*-methyl-*N*-phenylmannosylamine synthesised by these authors, and partly on the fact that no evidence could be obtained for the presence of the other possible isomer, 6-deoxy-2 : 3-di-*O*-methyl-L-idose. Complete methylation of (VII) proved difficult and the syrupy trimethyl ether

isolated was contaminated with breakdown products as shown by its negative rotation and the poor yield of aniline derivative. However, oxidation of this ether, followed by esterification and amide formation, gave crystalline 2 : 3 : 4-tri-*O*-methyl-L-arabaramide, proving that the syrupy trimethyl ether was in fact mainly 6-deoxy-2 : 3 : 4-tri-*O*-methylmannose.

The isolation of the 6-deoxy-L-idose in greater quantity from the unmethylated 3 : 4-epoxide does not support the statement by Bose, Chaudhuri, and Bhattacharyya (*Chem. and Ind.*, 1953, 869) that " the opening of the 3 : 4-epoxide ring seems to follow the rule that the hydroxyl group at position 4 must be *trans* to the bulky primary hydroxyl group " while the isolation of 6-deoxy-2 : 4-di-*O*-methylmannose (VII) from the 2-methyl-3 : 4-epoxide (III) is in agreement with these authors' contention. It may well be, however, that the methyl group, which in the present experiments has replaced the primary hydroxyl group, has less influence on the scission of the epoxide ring. At the same time these authors, in an extension of Fürst and Plattner's rule (*12th Int. Cong. Pure and Appl. Chem.*, 1951, *Abs.*, p. 409), express the view that the predominant product from the scission of the epoxide ring in 2 : 3-anhydro-sugars has the entering group in the axial position, and the isolation of 6-deoxy-3-*O*-methyl-L-idose (VI) from methyl 2 : 3-anhydro-6-deoxy-α-L-taloside (II) is in direct support of this view. This is not true however for the product (VIII) from the fission of methyl 2 : 3-anhydro-6-deoxy-4-*O*-methyl-α-L-taloside (IV), the entering group being equatorial (C1 conformation). It appears that the presence of a methoxyl group in the molecule has a definite directing effect in the scission of the epoxide ring.

A syrup with similar rotations and the same R_G value was obtained from the action of lithium aluminium hydride on the methyl 3 : 4- and 2 : 3-anhydro-6-deoxy-α-L-talosides, (I) and (II). Consideration of the formulæ of these two substances makes it clear that the product must be 3 : 6-dideoxytalose (3 : 6-dideoxyidose) (IX). As the reduction product from the 3 : 4-anhydro-2-*O*-methyl derivative (III) on demethylation gave a syrup with the same R_G as (IX) it may be tentatively assumed that this product is the 3 : 6-dideoxy-2-*O*-methyltalose. No conclusions can be drawn, from the evidence obtained, of the constitution of the main product from the action of lithium aluminium hydride on the 2 : 3-anhydro-4-*O*-methyl derivative (IV).

Experimental

All solvents were removed under reduced pressure and below 50°. The R_G values were determined with *n*-butanol–ethanol–water (4 : 1 : 5).

Methyl 3 : 4-*Anhydro*-6-*deoxy*-α-L-*taloside* (I).—An ethanolic (50 ml.) solution of methyl 4-*O*-toluene-*p*-sulphonyl-α-L-rhamnoside (20·0 g., from 25 g. of rhamnose hydrate), prepared according to the method described by Percival and Percival (*J.*, 1950, 690), was titrated with sodium hydroxide (2M; 30·0 c.c.) at 75° until it was permanently pink to phenolphthalein. Sodium toluenesulphonate was filtered off, and the solution evaporated to dryness. Extraction of the residue with dry ethyl acetate (5 × 20 c.c.) at room temperature, removal of the solvent, and recrystallisation of the residue from warm light petroleum (b. p. 40—60°) gave crystalline *methyl* 3 : 4-*anhydro*-6-*deoxy*-α-L-*taloside* (I) (8·0 g.), m. p. 68°, $[\alpha]_D^{15}$ −110° (*c*, 1·1 in H_2O) (Found : C, 52·7; H, 7·4. $C_7H_{12}O_4$ requires C, 52·5; H, 7·5%).

Alkaline Hydrolysis of Methyl 3 : 4-*Anhydro*-6-*deoxy*-α-L-*taloside*.—(a) *With barium hydroxide.* Crystalline (I) (0·05 g.) was heated with barium hydroxide (1 g.) in water (5 c.c.) at 100° for 2 hr. After suitable treatment a syrup (0·025 g.), $[\alpha]_D^{14}$ −60° (*c*, 0·4 in H_2O), was obtained (cf. methyl 6-deoxy-α-L-mannoside, $[\alpha]_D^{16}$ −62° in H_2O). Hydrolysis with N-sulphuric acid gave a reducing syrup which partly crystallised when kept. The crystals had m. p. 91° alone and admixed with 6-deoxy-L-mannose. Examination of the mother liquors on a paper chromatogram showed two discrete spots, R_G 0·40 and 0·50, identical with those of 6-deoxy-L-mannose and 6-deoxy-L-idose which were run as controls. The 6-deoxy-L-mannose was present in much the larger quantity.

(b) *With sodium methoxide.* (I) (2·5 g.) was heated at 80° for 19 hr. with dry methanol (150 c.c.) containing sodium methoxide [from sodium (2·0 g.)]. The solution was neutralised with solid carbon dioxide and evaporated to dryness. Extraction with chloroform (6 × 50 c.c.) and removal of the solvent gave a mobile syrup (2·0 g.), b. p. 120—130°/0·1 mm., n_D^{12} 1·4685, $[\alpha]_D^{16}$ −117° (*c*, 2·0 in H_2O). This (1·2 g.) was hydrolysed at 100° with N-sulphuric acid (52 c.c.) until the rotation became constant ($[\alpha]_D^{15}$ −40°; 4 hr.). Neutralisation of the solution with barium carbonate and evaporation to dryness gave a syrup (1·02 g.). Examination on a paper chroma-

togram showed two discrete spots, R_G 0·75 and 0·66, together with faint spots which corresponded to 6-deoxyidose, R_G 0·50, and 6-deoxymannose, R_G 0·40. The mixture was separated by passage through cellulose (Chanda, Hirst, and Percival, *J.*, 1951, 1240). Elution was by purified light petroleum (b. p. 100—120°)–*n*-butanol (1 : 1; v/v) saturated with water. Fraction 1*a* was a syrup (0·575 g., 56·9%), R_G 0·75, M_G 0·80 (Consden and Stanier, *Nature*, 1952, **170**, 1069; Foster and Stacey, *J. Appl. Chem.*, 1953, **3**, 19), $[\alpha]_D^{16}$ −14° (*c*, 0·7 in H_2O), −13° (*c*, 1·0 in EtOH), n_D^{18} 1·4790 (Found: C, 47·8; H, 8·6; OMe, 18·0. Calc. for $C_7H_{14}O_5$: C, 47·1; H, 7·9; OMe, 17·4%). In one experiment, crystals (0·045 g.) were obtained; they had m. p. 113—114°, R_G 0·75, M_G 0·80, $[\alpha]_D^{17}$ +14·4° (*c*, 2·5 in EtOH), −15° (constant) (*c*, 1·0 in H_2O) (Found: C, 46·8; H, 7·95; OMe, 17·2%). Appropriate treatment of fraction 1*a* (0·065 g.) gave 6-*deoxy*-3-*O*-*methyl*-N-*phenyl*-L-*idosylamine*, m. p. 62—63° (Found: C, 61·0; H, 8·0; N, 4·5. $C_{13}H_{19}O_4N$ requires C, 61·4; H, 7·9; N, 5·4%). Fraction 1*a* (30 mg.) in water (2 c.c.), phenylhydrazine (0·15 c.c.), and glacial acetic acid (2 drops) was heated at 100° for 2 hr. in an atmosphere of carbon dioxide. The solid obtained on cooling was recrystallised from aqueous ethanol, giving pale yellow needles of 6-*deoxy*-3-O-*methyl*-L-*idosazone*, m. p. 122—123°, $[\alpha]_D^{16}$ −60° (*c*, 1·6 in EtOH) (Found: OMe, 8·4; N, 14·9. $C_{19}H_{24}O_3N_4$ requires OMe, 8·7; N, 15·8%). Fraction 2*a* was a syrup (0·270 g., 26·8%), R_G 0·66, which crystallised completely when kept; the solid had R_G 0·65, M_G 0·58, m. p. 122°, $[\alpha]_D^{15}$ +15° (*c*, 1·0 in MeOH) (Found: C, 47·2; H, 8·1; OMe, 17·2. Calc. for $C_7H_{14}O_5$: C, 47·2; H, 7·9; OMe, 17·4%). Levene and Muskat (*J. Biol. Chem.*, 1934, **105**, 431) record m. p. 122° and $[\alpha]_D$ +13° (in MeOH) for 6-deoxy-4-*O*-methylmannose. Fraction 3*a*, a syrup (0·051 g., 5·05%), had R_G 0·50, $[\alpha]_D^{16}$ −27·4° (*c*, 1·5 in H_2O). Meyer and Reichstein (*Helv. Chim. Acta*, 1946, **29**, 149) record $[\alpha]_D^{15}$ −26° (*c*, 4·462 in H_2O) for 6-deoxy-L-idose. Fraction 4*a* (0·060 g., 5·9%), R_G 0·40, crystallised completely and then had m. p. 92—94°, alone and mixed with authentic 6-deoxymannose.

Methyl 3 : 4-*Anhydro*-6-*deoxy*-2-O-*methyl*-α-L-*taloside* (III).—Crystalline methyl 3 : 4-anhydro-6-deoxy-α-L-taloside (I) (3·0 g.) was methylated four times with methyl iodide and silver oxide, and a mobile syrup (2·8 g.) was isolated, which distilled at 80—100°/0·01 mm. and had n_D^{16} 1·4500, $[\alpha]_D^{15}$ −140° (*c*, 0·6 in MeOH) (Found: OMe, 35·8. $C_8H_{14}O_4$ requires OMe, 35·6%).

Alkaline hydrolysis with sodium methoxide. Following the procedure used for the unmethylated material the syrup (III) (3·80 g.) was treated with sodium methoxide solution (250 c.c.). A mobile syrup (3·73 g.), $[\alpha]_D^{16}$ −60° (*c*, 1·0 in H_2O), was obtained. This was hydrolysed with N-sulphuric acid to constant rotation ($[\alpha]_D^{16}$ −12°; 3 hr.), and a syrup (*A*) (3·2 g.) which partly crystallised on storage at 0° was obtained. The crystals (VII) (1·17 g.) had m. p. 82°, $[\alpha]_D^{16}$ −19° (*c*, 1·0 in H_2O), +14·5° ⟶ −3° (48 hr. constant) (*c*, 1·8 in EtOH) (Found: C, 49·5; H, 8·1; OMe, 31·7. Calc. for $C_8H_{16}O_5$: C, 49·9; H, 8·4; OMe, 32·3%). The mother liquors (2·03 g.) from (*A*) on chromatographic analysis showed a main spot, R_G 0·86, and a fainter spot, R_G 1·0. Purification, by passage through powdered cellulose as described previously, gave a further yield of crystals (VII) (0·8 g.), m. p. 82°, a residual syrup (*B*), R_G 0·86, (0·81 g.), and a small quantity of a second fraction, R_G 1·0, $[\alpha]_D$ +20° (*c*, 0·05 in H_2O).

Characterisation of 6-*Deoxy*-2 : 4-*di*-O-*methylmannose*.—The crystals (VII) (0·05 g.) were demethylated by hydriodic acid (2 c.c.) at 100° for 10 min. A syrup which on chromatographic analysis gave a single spot identical with that given by 6-deoxymannose was isolated. Demethylation of syrup (*B*) which was chromatographically and ionophoretically identical with the crystals (VII) gave rise to a similar syrup which revealed only the presence of 6-deoxymannose.

The crystals (VII) (100 mg.) were oxidised with bromine water (1 c.c.) at 15° for 96 hr. The lactone (75 mg.), isolated in the usual way, had $[\alpha]_D^{15}$ +47° (*c*, 0·9 in H_2O) unchanged after 70 hr.; it failed to crystallise or to yield a crystalline amide or phenylhydrazide.

The crystals (VII) (0·1 g.) were heated at 80° for 6 hr. with ethanol (6 c.c.) containing aniline (0·55 c.c.) in the presence of Drierite (0·2 g.). Removal of the solvent at room temperatures gave 6-deoxy-2 : 4-di-*O*-methyl-*N*-phenylmannosylamine, m. p. 141—142°, $[\alpha]_D^{16}$ +110° ⟶ +7° (20 hr.) (*c*, 0·4 in EtOH) (Found: C, 60·8; H, 7·5; OMe, 23·3; N, 5·4. Calc. for $C_{14}H_{21}O_4N$: C, 62·9; H, 7·9; OMe, 23·2; N, 5·2%). An *X*-ray powder photograph of this aniline derivative obtained through the courtesy of Dr. C. A. Beevers was pronounced identical with one of 6-deoxy-2 : 4-di-*O*-methyl-*N*-phenylmannosylamine synthesised in the Birmingham laboratories and supplied by Professor M. Stacey, F.R.S. (*Chem. and Ind.*, 1954, 107). The residual syrup (*B*) gave an identical aniline derivative, m. p. 141—142° alone and mixed with the derivative prepared from the crystals.

The dimethyl sugar (VII) (0·165 g.) was converted into the glycoside (0·150 g.) with 1%-methanolic hydrogen chloride, and this was followed by four methylations with methyl iodide

and silver oxide. A mobile syrup (0·145 g.), n_D^{16} 1·4421, $[\alpha]_D^{16}$ −17° (*c*, 1·5 in H_2O), was isolated. Hirst and Macbeth (*J.*, 1926, 22) record n_D^{15} 1·4423, $[\alpha]_D^{16}$ −15° (in H_2O), for methyl 6-deoxy-2 : 3 : 4-tri-*O*-methyl-L-mannoside (Found : OMe, 55·6. Calc. for $C_{10}H_{20}O_4$: OMe, 56·3%). Hydrolysis with N-sulphuric acid gave a syrup, $[\alpha]_D^{17}$ −12° (*c*, 0·5 in H_2O), −24° (*c*, 0·8 in EtOH) {Hirst and Macbeth, *loc. cit.*, record $[\alpha]_D$ +25° (in H_2O), −9° (in ethanol), for 6-deoxy-2 : 3 : 4-tri-*O*-methyl-L-mannose}, which on chromatographic analysis gave a single discrete spot (R_G 1·01) identical with the spot given by authentic 6-deoxy-2 : 3 : 4-tri-*O*-methyl-L-mannose. Attempted conversion into 6-deoxy-2 : 3 : 4-tri-*O*-methyl-*N*-phenylmannosylamine gave a very poor yield of crystals, m. p. and mixed m. p. 111—112°.

Oxidation of the trimethyl ether (0·30 g.) with nitric acid (5·5 c.c.; *d*, 1·42) (Mullan and Percival, *J.*, 1940, 1505) gave a syrup (0·06 g.) which was esterified with boiling methanolic hydrogen chloride (2%; 3·5 c.c.) for 6 hr. The derived amide, $[\alpha]_D^{16}$ +52° (*c*, 0·5 in EtOH), partly crystallised, m. p. and mixed m. p. 230°. Hirst and Macbeth (*loc. cit.*) record $[\alpha]_D^{16}$ +50·4° (in H_2O) for 2 : 3 : 4-tri-*O*-methyl-L-arabaramide.

Methyl 2 : 3-*Anhydro*-6-*deoxy*-α-L-*taloside* (II).—Crystalline methyl 6-deoxy-2-*O*-toluene-*p*-sulphonyl-α-L-galactoside (3·30 g.), prepared from 6-deoxygalactose by Percival and Percival's method (*loc. cit.*), was titrated with sodium hydroxide (2M; 9 c.c.) as described for the corresponding 6-deoxymannose derivative. Removal of ethyl acetate gave an extremely volatile crystalline product (II) (1·70 g.) which after recrystallisation from ethanol had m. p. 95—97°, $[\alpha]_D^{16}$ −88° (*c*, 2·0 in H_2O) (Found : C, 52·45; H, 7·3. $C_7H_{12}O_4$ requires C, 52·5; H, 7·5%). This *taloside* was very soluble in alcohol, acetone, chloroform, and light petroleum.

Alkaline hydrolysis. Hydrolysis of (II) with sodium methoxide as described above gave a syrup (0·32 g. from 0·35 g.). Removal of the glycosidic group with N-sulphuric acid afforded a syrup (*C*) (0·21 g.) which on chromatographic analysis showed two spots, R_G 0·75 and 0·50. Separation on cellulose gave two fractions. Fraction 1*b* was a syrup (0·150 g.), $[\alpha]_D^{16}$ −14° (*c*, 0·7 in H_2O) (Found : OMe, 17·5. Calc. for $C_7H_{14}O_5$: OMe, 17·4%), which was chromatographically and ionophoretically identical with fraction I*a*, obtained by similar treatment of the 3 : 4-anhydro-derivative. 6-Deoxy-3-*O*-methyl-*N*-phenyl-L-idosylamine, m. p. and mixed m. p. 62—63°, and 6-deoxy-3-*O*-methyl-*N*-phenyl-L-idosazone, m. p. and mixed m. p. 122—123°, were also prepared from fraction I*b*. Fraction 2*b*, a syrup (0·030 g.; 15%), $[\alpha]_D^{16}$ −22° (*c*, 1·0 in H_2O), R_G 0·50, was presumed to be 6-deoxy-2-*O*-methylgalactose. Nucleation, however, failed to induce crystallisation, and chromatographic comparison showed that authentic 6-deoxy-2-*O*-methylgalactose has R_G 0·59. Paper ionophoresis of 6-deoxy-2-*O*-methylgalactose gave M_G 0·33 while fraction 2*b* gave M_G 1·0 and 6-deoxygalactose 0·92. 6-Deoxy-L-idose (fraction 3*a*) had R_G 0·59, M_G 1·0.

Methyl 2 : 3-*Anhydro*-6-*deoxy*-4-O-*methyl*-α-L-*taloside* (IV).—(II) (1·01 g.) was methylated four times with methyl iodide and silver oxide. Recrystallisation of the *taloside* (IV) from acetone–light petroleum (b. p. 40—60°) gave long needles, m. p. 108—110°, $[\alpha]_D^{16}$ ±0° (*c*, 0·7 in EtOH, $CHCl_3$, and $COMe_2$) (Found : C, 54·7; H, 8·1; OMe, 35·0. $C_8H_{14}O_4$ requires C, 55·2; H, 8·1; OMe, 35·6%).

Alkaline hydrolysis. Methyl 2 : 3-anhydro-6-deoxy-4-*O*-methyl-α-L-taloside (IV) (0·90 g.) was hydrolysed with sodium methoxide as described for the 3 : 4-anhydro-derivative. The resultant syrup (0·70 g.) after hydrolysis with sulphuric acid had $[\alpha]_D^{18}$ −15° (*c*, 2·4 in MeOH) and gave, on chromatographic analysis, a single spot R_G 0·80 (Found : OMe, 31·8. $C_8H_{16}O_5$ requires OMe, 32·3%).

Characterisation of the syrupy dimethyl compound, R_G 0·80. Demethylation of a portion (0·050 g.) of the syrup with hydriodic acid (*d*, 1·7; 2 c.c.) gave a product which was chromatographically indistinguishable from 6-deoxy-L-galactose.

The syrup, R_G 0·80 (0·235 g.), was converted into the glucoside by methanolic hydrogen chloride (2%; 24 c.c.) at 80°, until it did not reduce Fehling's solution (3 hr.). The glycoside, $[\alpha]_D^{16}$ −30° (*c*, 1·5 in EtOH), was methylated five times with methyl iodide and silver oxide; the resultant methyl tri-*O*-methylglycoside crystallised spontaneously. The crystals (0·15 g.) had m. p. and mixed m. p. 93—95°, $[\alpha]_D^{16}$ −200° (*c*, 1·0 in H_2O) (Found : C, 54·05; H, 9·1; OMe, 55·4. Calc. for $C_{10}H_{20}O_5$: C, 54·55; H, 9·1; OMe, 56·3%) [James and Smith, *J.*, 1945, 746, record m. p. 85—92°, $[\alpha]_D$ −196° (*c*, 0·5 in H_2O), for methyl 6-deoxy-2 : 3 : 4-tri-*O*-methyl-α-L-galactoside.]

Dideoxy-sugars derived by the Action of Lithium Aluminium Hydride on Methyl Anhydro-6-deoxytalosides.—Each of the above anhydro-derivatives (I—IV) was treated with lithium aluminium hydride, and the products examined chromatographically. All attempts to prepare crystalline aniline derivatives, phenylosazones, and toluene-*p*-sulphonyl derivatives failed.

A typical reduction was carried out as follows. Crystalline methyl 3 : 4-anhydro-6-deoxy-α-L-taloside (I) (2·0 g.) in dry ether (150 c.c.) was added dropwise during 45 min. to a gently refluxing suspension of finely powdered lithium aluminium hydride (2·0 g.) in dry ether (150 c.c.) under vigorous stirring, and the reaction allowed to continue a further 4 hr. The flask was cooled in ice-water, excess of lithium aluminium hydride destroyed by the careful addition of water, and the mixture made acid (2N-sulphuric acid). Exhaustive extraction with chloroform (10 × 100 c.c.) afforded, after purification with Filter Cel, a syrup (0·7 g.) which was hydrolysed with N-sulphuric acid; the resultant reducing syrup showed a single discrete spot on chromatographic analysis.

Similar treatment of the other anhydro-derivatives (II—IV) gave syrups contaminated with 6-deoxy-idose and -galactose and separation on cellulose was necessary. In addition the methylated anhydro-sugars (III) and (IV) also gave some of the products isolated from (I) and (II). The constants of the main products after separation were :

Product from methyl 6-deoxy-α-L-taloside	Yield, %	$[\alpha]_D^{16}$ in MeOH	$[\alpha]_D^{16}$ in H_2O	OMe, %	R_G
3 : 4-Anhydro-	38	−20°	−16°	—	0·72
2 : 3-Anhydro-	11	−18	−20	—	0·72
3 : 4-Anhydro-2-*O*-methyl-	17	−14	− 4	19·2	0·90
2 : 3-Anhydro-4-*O*-methyl-	20	−25	−38	18·7	0·93

Demethylation of the syrup, R_G 0·90, gave a chromatographically pure syrup, R_G 0·72.

Application of the Dische test (Dische, *Mikrochem.*, 1930, **8**, 4; Deriaz, Stacey, Teece, and Wiggins, *J.*, 1949, 1222), as extended by Allerton, Overend, and Stacey (*J.*, 1952, 255) to 3-deoxyxylose and 2 : 3-dideoxyribose, to these dideoxy-derivatives gave values for the molecular extinction coefficients which were in reasonable agreement with those obtained by the last authors.

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