The Methyl 2,3-Anhydrolyxopyranosides and 3,4-Anhydroarabinopyranosides

By J. G. Buchanan and R. Fletcher

Monotoluene-*p*-sulphonylation of methyl α-D-xylopyranoside gives mainly the 2-sulphonate, which yields a mixture of methyl 2,3-anhydro-α-D-lyxopyranoside and methyl 3,4-anhydro-α-D-arabinopyranoside on treatment with alkali. At equilibrium the anhydroarabinoside predominates in the ratio 71 : 29. Methyl 2,3-anhydro-β-L-lyxopyranoside and methyl 3,4-anhydro-β-L-arabinopyranoside have been prepared from methyl β-L-arabinopyranoside, and their equilibration has been studied; the anhydrolyxoside predominates in the ratio 68 : 32. These results are compared with other cases of epoxide migration. When the acetates of the four epoxides are hydrolysed by aqueous acetic acid, unidirectional opening of the oxide ring occurs owing to the presence of a neighbouring *trans*-acetoxy group.

As part of a study of epoxide migration and neighbouring-group reactions in vicinal epoxides,[1] we wished to examine the methyl anhydropentopyranosides. The compounds of interest to us have a hydroxyl group vicinal and *trans* to the three-membered oxide ring, *i.e.*, the 2,3-anhydrolyxopyranosides (IX) and (XIV) or their enantiomers and the 3,4-anhydroarabinopyranosides (VII) and (XI) or their enantiomers. One of these, methyl 2,3-anhydro-β-L-lyxopyranoside (XIV), has been synthesised by Reist *et al.*[2] concurrently with the present work; our failure to prepare it by Honeyman's method [3] is discussed later. Jones and his coworkers [4] studied epoxide migrations in this series but the anhydro-compounds were not fully characterised.

Methyl α-D-xylopyranoside (II) was selected as a suitable starting material since Ferrier and his coworkers have established an excellent method for its preparation.[5] Initially we received a very generous gift of the phenylboronate from Dr. Ferrier. Monotoluene-*p*-sulphonylation gave mainly a monosulphonate A, m. p. 135—136°, most of which could be isolated by crystallisation of the crude product. Chromatography of the remainder on silica gel gave more of A together with a second crystalline sulphonate B, m. p. 57—58°. Since A and B each reduced 1 mol. of periodate, one of them was the 2-sulphonate (III) and the other the 4-sulphonate (I). When A was hydrolysed with aqueous sodium hydroxide and the products examined by paper chromatography methyl α-D-arabinopyranoside (IV) and methyl α-D-lyxopyranoside (XVII) were formed in about equal quantities, together with traces of the two xylopyranosides (II) and (XVI). Compound A was thus the 2-sulphonate (III), and the pentopyranosides arose by hydrolysis of the intermediate anhydro-compounds (IX) and (XI). When B was treated in similar fashion, methyl α-D-xylopyranoside (II) and methyl β-L-arabinopyranoside (XXIV) were the major products, together with methyl β-L-lyxopyranoside (VI); none of the other possible product, the xylopyranoside (XVI), could be detected. Compound B can thus be assigned independently the structure (I), which is capable of yielding the anhydro-compounds (VII) and (XIV). Further work on the anhydro-compounds themselves fully substantiated these assignments. Preferential acylation of the C-2 hydroxyl group of methyl α-D-xylopyranoside is consistent with the formation of 2,6-di-*O*-acyl derivatives from the reaction of methyl α-D-glucopyranoside with limited amounts of benzoyl chloride,[6] methanesulphonyl chloride,[7] or toluene-*p*-sulphonyl chloride [8] in pyridine.

Treatment of the 2-sulphonate (III) with sodium methoxide in methanol resulted in the formation of methyl 2,3-anhydro-α-D-lyxopyranoside (IX) and methyl 3,4-anhydro-α-D-arabinopyranoside (XI). Thin-layer chromatography (t.l.c.) indicated that epoxide migration had occurred before all the sulphonate had reacted. Adsorption chromatography was used to separate these two anhydro-compounds, both of which crystallised. It was possible to assign the structures of the two

[1] J. G. Buchanan, *J. Chem. Soc.*, 1958, 955, and subsequent Papers.
[2] E. J. Reist, L. V. Fisher, and D. E. Gueffroy, *J. Org. Chem.*, 1966, **31**, 226.
[3] J. Honeyman, *J. Chem. Soc.*, 1946, 990.
[4] J. K. N. Jones, M. B. Perry, and J. C. Turner, *Canad. J. Chem.*, 1960, **38**, 1122.
[5] R. J. Ferrier, D. Prasad, A. Rudowski, and I. Sangster, *J. Chem. Soc.*, 1964, 3330.
[6] T. Lieser and R. Schweizer, *Annalen*, 1935, **519**, 271; R. E. Reeves, *J. Amer. Chem. Soc.*, 1948, **70**, 259.
[7] A. K. Mitra, D. H. Ball, and L. Long, jun., *J. Org. Chem.*, 1962, **27**, 160.
[8] J. Jarý, K. Čapek, and J. Kovář, *Coll. Czech. Chem. Comm.*, 1964, **29**, 930.

anhydro-compounds because the first product of alkali treatment, necessarily the anhydrolyxoside (IX), had the higher R_F value on t.l.c. The anhydrolyxoside (IX) afforded a syrupy acetate (X) which was treated with 80% acetic acid at 100°. Because of the neighbouring *trans*-acetoxy group,[9] only α-D-arabinopyranosides would be expected as products. A crystalline monoacetate (V) of methyl α-D-arabinopyranoside was isolated, and only the arabinoside (IV) could be detected on chromatography of the deacetylated mother-liquors. The acetate (V) reduced 1 mol. of sodium periodate and could be deacetylated to the triol (IV). Similarly, the anhydroarabinoside (XI) yielded a crystalline acetate (XII) which, on acid hydrolysis, gave only monoacetates of methyl α-D-lyxopyranoside (XVII).

Methyl 4-*O*-toluene-*p*-sulphonyl-α-D-xyloside (I) yielded crystalline methyl 3,4-anhydro-β-L-arabinopyranoside (VII) on treatment with sodium methoxide. The formation of this anhydro-compound occurred more rapidly than the formation of the 2,3-anhydrolyxoside (IX) from the 2-sulphonate (III). Thin-layer chromatography indicated complete conversion of the sulphonate (I) into the anhydroarabinoside (VII) before any appreciable epoxide migration had occurred. The crystalline acetate (VIII) was hydrolysed with acetic acid, to give only derivatives of methyl β-L-lyxopyranoside (VI), characterised as the triacetate.

Treatment of the 4-sulphonate (I) with sodium methoxide was not a convenient method for preparing the anhydro-compounds (VII) and (XIV) because of the difficulty in obtaining even small amounts of the pure sulphonate. Another route has been developed from methyl β-L-arabinopyranoside (XXIV). Condensation with acetone gave the ketal (XX) [3] whose benzoate (XXI) [3] was hydrolysed to the diol (XVIII).[3,10] Monotoluene-*p*-sulphonylation followed by acetylation afforded a crystalline monosulphonate, which readily yielded a mixture of anhydro-compounds on treatment with sodium methoxide. This was strong evidence that

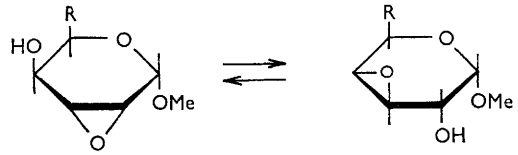
[9] J. G. Buchanan and J. C. P. Schwarz, *J. Chem. Soc.*, 1962, 4770.

[10] M. A. Oldham and J. Honeyman, *J. Chem. Soc.*, 1946, 986.

the sulphonate was the 3-*O*-toluene-*p*-sulphonylarabinoside (XIII) rather than the 4-sulphonate, and it was confirmed when one of the anhydro-compounds proved to be identical with the anhydroarabinoside (VII) prepared from the 4-*O*-toluene-*p*-sulphonylxyloside (I). The other anhydro-compound, which was also crystalline, was shown to be the anhydrolyxoside (XIV) when its acetate (XV) yielded only methyl 4-*O*-acetyl-β-L-arabinopyranoside (XXV) on acid hydrolysis (cf. ref. 11). Reist *et al.*[2] also found that monotoluene-*p*-sulphonylation of the benzoate (XVIII) occurs preferentially on the equatorial C-3 hydroxyl group, and that the anhydrolyxoside (XIV) could be prepared in this way.

Honeyman[3] described the preparation of syrupy methyl 2,3-anhydro-β-L-lyxopyranoside (XIV) and its crystalline acetate (XV) by the following route. The acetate (XXII) was hydrolysed with acid to give the diol (XIX), m. p. 172°, $[\alpha]_D$ +252·2°, which yielded the disulphonate (XXIX), m. p. 62—63°, $[\alpha]_D$ +173·2°, on treatment with toluene-*p*-sulphonyl chloride in pyridine. Alkaline methanolysis of the disulphonate gave the anhydro-compound (XIV), $[\alpha]_D$ +127·6 whose crystalline acetate (XV) had m. p. 112—114°, $[\alpha]_D$ +106·9°. The physical properties of the final products do not correspond to those of any of our anhydro-compounds, even allowing for epoxide migration, and the products of alkaline hydrolysis (methyl β-L-xylopyranoside and methyl β-L-arabinopyranoside) do not agree with those in the present work. In our hands acid hydrolysis of the acetate (XXII) under Honeyman's conditions gave methyl β-L-arabinopyranoside (XXIV) as the only crystalline product. Under milder conditions the syrupy 2-acetate (XIX) was obtained, which yielded the ester (XXIX), m. p. 178—179°, $[\alpha]_D$ +149°, on toluene-*p*-sulphonylation. Alkali treatment of this disulphonate under the reported conditions[3] did not yield an anhydro-compound free from the toluene-*p*-sulphonyl group. When methyl β-L-arabinopyranoside itself was treated with toluene *p*-sulphonyl chloride (2 mol.) the major product did not crystallise but was shown to be the 2,3-disulphonate (XXVI) by conversion into the crystalline acetate (XXVII). The latter was prepared independently from the 2-sulphonate (XXX), which was itself derived from the ketal (XXIII),[3] and from the 4-acetate (XXV). The 2,3,4-trisulphonate (XXVIII) was also prepared during this work, which was discontinued when other methods were found to yield the required anhydro-compounds.

One of our objectives was to study the interconversion of the two pairs of anhydro-compounds, (XIV) and (VII) and (IX) and (XI), under alkaline conditions. In both cases the specific rotations were sufficiently different for polarimetry[12] to be used to determine the position of equilibrium. Approximately 0·05M-solutions of each anhydro-compound in 0·05M-sodium hydroxide were studied polarimetrically. At equilibrium the ratio of anhydrolyxoside (XIV) to anhydroarabinoside (VII) was 68 : 32; that of anhydrolyxoside (IX) to anhydroarabinoside (XI) was 29 : 71. Each pair of anhydro-compounds belongs to one of two series which have been examined by Jarý and Čapek,[13] by Jarý, Čapek, and Kovář,[8] and by ourselves.[9,11] The epoxides (XIV) and (VII) belong to series 1, and it is noteworthy that in all the examples in this series[11,13] the 2,3-epoxide

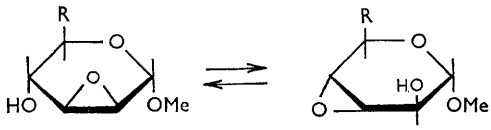


R = H, Me,[13] CH_2·O·CH_2Ph,[11] CH_2·O·CPh_3[11]

Series 1

is the more stable (*K ca.* 1·5—2). This may imply that all these compounds have half-chair conformations resembling the C1 conformation of the pyranose ring with the R group equatorial or pseudoequatorial.

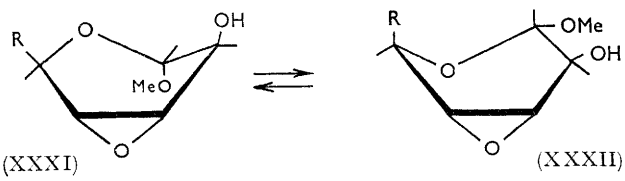
The epoxides (IX) and (XI) belong to series 2. In the previous cases examined[8,9] the equilibrium strongly favoured the 2,3-epoxide (*K* >9). This has been interpreted as being due to the instability of the 3,4-



R = H, Me,[8] CH_2·OH,[9] CH_2·O·CPh_3[9]

Series 2

epoxide, as a consequence either of the pseudoaxial C-2 hydroxyl group [in conformation (XXXI)] or the pseudoaxial R group [in conformation (XXXII)].[9] It is therefore interesting that when R is hydrogen the position of equilibrium is reversed (*K ca.* 0·4). This may be due to the relative stability of conformation (XXXII) in the case of the anhydroarabinoside (XI). It is hoped to settle some of these questions by a study of the conformations of compounds in both series by n.m.r. spectroscopy.



EXPERIMENTAL

Infrared spectra were measured for potassium bromide discs. Light petroleum refers to the fraction of b. p. 40—60°. Comparison of materials with authentic substances was made, unless stated otherwise, by mixed m. p. determinations and infrared spectra. Specific rotations refer to room temperature (20—25°). Removal of solvents by distillation was always carried out under reduced pressure.

[11] J. G. Buchanan and R. Fletcher, *J. Chem. Soc.*, 1965, 6316.
[12] S. J. Angyal and P. T. Gilham, *J. Chem. Soc.*, 1957, 3691.
[13] J. Jarý and K. Čapek, *Coll. Czech. Chem. Comm.*, 1966, **31**, 315.

80% Acetic acid refers to acetic acid–water (4 : 1 v/v). Quantitative periodate oxidations were performed using the spectrophotometric method.[14]

Adsorption chromatography was carried out using silica gel (Hopkin and Williams). Thin-layer chromatography (t.l.c.) used Kieselgel G (Merck) as adsorbent; carbohydrates were detected wth anisaldehyde–sulphuric acid,[15] and toluene-*p*-sulphonates by alcoholic diphenylamine, followed by exposure of the plate to u.v. light.[16] Paper chromatography was carried out on Whatman No. 1 paper using butan-2-one saturated with water as solvent; chromatograms were pre-equilibrated with solvent vapour for 1 hr. before irrigation. Vicinal epoxides were detected by sodium iodide and Methyl Red,[9] and vicinal glycols by periodate and Schiff's reagent.[17] R_F values are given in Table 1; better separations of pentopyranosides were achieved by allowing the solvent to overrun the end of the paper.

TABLE 1

Methyl glycoside	R_F value
α-D-Arabinopyranoside	0·13
β-L-Arabinopyranoside	0·15
β-D-Lyxopyranoside	0·18
β-D-Xylopyranoside	0·21
α-D-Xylopyranoside	0·22
α-D-Lyxopyranoside	0·30
2,3-Anhydro-β-L-lyxopyranoside	0·73
3,4-Anhydro-β-L-arabinopyranoside	0·77
3,4-Anhydro-α-D-arabinopyranoside	0·81
2,3-Anhydro-α-D-lyxopyranoside	0·88

*Toluene-*p*-sulphonates.—Toluene-*p*-sulphonylation of methyl α-D-xylopyranoside.* Methyl α-D-xylopyranoside (6·0 g.) was dissolved in pyridine (25 ml.) and treated with toluene-*p*-sulphonyl chloride (7·0 g., 1·0 mol.) at 0—5°. After 48 hr. at room temperature the product was isolated using chloroform. When the resulting syrup was treated with benzene (80 ml.) *methyl* 2-O-*toluene*-p-*sulphonyl*-α-D-*xylopyranoside* (3·1 g., 27%) crystallised, m. p. 130—134°. Recrystallised from water or benzene it had m. p. 135—136°, $[\alpha]_D$ +85·9° (*c* 0·55 in chloroform) (Found: C, 49·0; H, 5·4. $C_{13}H_{18}O_7S$ requires C, 49·1; H, 5·65%). The 2-sulphonate reduced periodate as follows: 0·23 mol. (1 day); 0·63 mol. (6 days); 0·88 mol. (15 days); 0·98 mol. (20 days). On acetylation with acetic anhydride and pyridine, the 2-sulphonate yielded a *diacetate*, m. p. 143—144° (from ethanol) (Found: C, 50·8; H, 5·4. $C_{17}H_{22}O_9S$ requires C, 50·75; H, 5·5%).

The benzene mother-liquors, above, were examined by t.l.c. using ethyl acetate as solvent. Disulphonates and three monosulphonates of methyl xyloside were detected. The mixture was chromatographed on silica gel (100 g.). Benzene–ether (3 : 1) eluted a mixture of disulphonates which was not examined further. Benzene–ether (3 : 2) eluted a syrupy monosulphonate (25 mg.; probably the 3-isomer) followed by the 2-sulphonate which crystallised from benzene (2·3 g., 20%), m. p. 132—134°. Further elution afforded the 4-*sulphonate* (0·45 g., 4%), m. p. 57—58°, $[\alpha]_D$ +97·1° (*c* 0·48 in chloroform), after crystallisation from benzene and then water (Found: S, 10·4%). The 4-sulphonate reduced periodate as follows: 0·42 mol. (1 day); 0·64 mol. (6 days); 0·87 mol. (15 days); 0·96 mol. (20 days).

Alkaline hydrolysis of methyl α-D-*xylopyranoside* 2- *and* 4-*toluene*-p-*sulphonate.* (*a*) The 2-sulphonate (10 mg.) was heated with N-sodium hydroxide (0·2 ml.) in a sealed tube at 100° for 2 hr. The solution was diluted with water, passed through a short column of Dowex 50(NH_4^+ form) resin, and the eluate evaporated to dryness. The residue was examined by paper chromatography. Methyl α-D-arabinopyranoside and methyl α-D-lyxopyranoside were present in about equal quantities, as shown by periodate and Schiff's reagent. Traces of methyl α-D- and β-L-xylopyranoside were detected.

(*b*) The 4-sulphonate (12 mg.) was treated as in (*a*). The products were methyl β-L-arabinopyranoside and methyl α-D-xylopyranoside in about equal amounts as the major products, together with some methyl β-L-lyxopyranoside. No methyl β-L-xylopyranoside was detected.

Methyl 4-O-*acetyl*-2-O-*benzoyl*-3-O-*toluene*-p-*sulphonyl*-β-L-*arabinopyranoside.* Methyl 2-*O*-benzoyl-β-L-arabinopyranoside [3] (2·0 g.) was dissolved in pyridine (16 ml.), and toluene-*p*-sulphonyl chloride (1·42 g., 1 mol.) added with cooling. After 24 hr. at room temperature, pyridine (10 ml.) and acetic anhydride (8 ml.) were added and the mixture was left at room temperature overnight. The product was isolated using chloroform, to give the *sulphonate* (1·67 g., 48%), m. p. 165—166° (from methanol), $[\alpha]_D$ +200° (*c* 0·44 in chloroform) (Found: C, 56·8; H, 5·4. $C_{22}H_{24}O_9S$ requires C, 57·0; H, 5·2%).

Anhydro-compounds in the α-D-*Series.—Methyl* 2,3-*anhydro*-α-D-*lyxopyranoside and* 3,4-*anhydro*-α-D-*arabinopyranoside.* Methyl 2-*O*-toluene-*p*-sulphonyl-α-D-xylopyranoside (9·36 g.) was dissolved in methanol (130 ml.) containing sodium methoxide (from 0·75 g. of sodium; *ca.* 2 mol.) and kept at 55—60° for 1 hr. The solution was neutralised with 2N-sulphuric acid and evaporated to dryness. The residue was extracted with boiling benzene (3 × 150 ml.), and the combined extracts were evaporated, leaving a colourless syrup. The syrup was dissolved in benzene (200 ml.) and chromatographed on silica gel (200 g.). Benzene–ether (4 : 1) eluted the *anhydrolyxoside* (2·97 g., 67%), m. p. 62—63°, $[\alpha]_D$ +111° (*c* 0·88 in water), crystallised from light petroleum and ethyl acetate–light petroleum (Found: C, 49·0; H, 6·7. $C_6H_{10}O_4$ requires C, 49·3; H, 6·85%). Benzene–ether (1 : 1) eluted the *anhydroarabinoside* (0·64 g., 14·8%), m. p. 95—96°, $[\alpha]_D$ +65·6° (*c* 0·78 in water), crystallised from light petroleum and ethyl acetate–light petroleum (Found: C, 49·3; H, 6·8%).

Methyl 4-O-*acetyl*-2,3-*anhydro*-α-D-*lyxopyranoside.* The above anhydrolyxoside (0·81 g.) was acetylated overnight using pyridine (8 ml.) and acetic anhydride (4 ml.). The product was isolated by means of chloroform, giving the syrupy *acetate* (0·88 g., 86%), $[\alpha]_D$ +88·6° (*c* 1·21 in chloroform) (Found: C, 51·1; H, 6·3. $C_8H_{12}O_5$ requires C, 51·1; H, 6·4%).

Acid hydrolysis of methyl 4-O-*acetyl*-2,3-*anhydro*-α-D-*lyxopyranoside.* The acetate (0·15 g.) was heated in 80% acetic acid (1·3 ml.) at 100° for 20 min. Evaporation of the solvent left *methyl* 4-O-*acetyl*-α-D-*arabinopyranoside* as a syrup which crystallised on standing. Recrystallisation from ethyl acetate gave the monoacetate as needles (98 mg., 57%), m. p. 110—111°, $[\alpha]_D$ −20·5° (*c* 0·64 in chloroform) (Found: C, 46·6; H, 6·8. $C_8H_{14}O_6$ requires C, 46·6; H, 6·8%). The acetate reduced periodate as follows: 0·44 mol.

[14] G. O. Aspinall and R. J. Ferrier, *Chem. and Ind.*, 1957, 1216.
[15] E. Stahl and U. Kaltenbach, *J. Chromatog.*, 1961, **5**, 351.
[16] M. Jackson and L. D. Hayward, *J. Chromatog.*, 1961, **5**, 166.
[17] J. Baddiley, J. G. Buchanan, R. E. Handschumacher, and J. F. Prescott, *J. Chem. Soc.*, 1956, 2818.

(4 hr.); 0·77 mol. (10 hr.); 1·04 mol. (24 hr.); 1·10 mol. (48 hr.). The mother-liquor from the crystallisation was evaporated, and the residue deacetylated with sodium methoxide in methanol. Only methyl α-D-arabinoside could be detected by periodate and Schiff's reagent after paper chromatography.

Deacetylation of methyl 4-O-*acetyl*-α-D-*arabinopyranoside*. The acetate (87 mg.) was dissolved in methanol (4 ml.) containing sodium methoxide (from 1 mg. of sodium) and kept at room temperature for 5 hr. The solution was diluted with water, passed through a column of Dowex 50 (NH_4^+ form), resin, and the eluate evaporated to dryness. The crystalline residue was recrystallised from ethyl acetate, to give methyl α-D-arabinopyranoside (47 mg., 69%), m. p. 124—126°, $[\alpha]_D$ −17·0° (*c* 0·74 in water), identical with an authentic sample.

Methyl 2-O-*acetyl*-3,4-*anhydro*-α-D-*arabinopyranoside*. The above 3,4-anhydro-α-D-arabinoside (0·46 g.) was acetylated, and the product isolated in the same way as for the anhydrolyxoside. The *acetate* (0·45 g., 77%), m. p. 107—108°, $[\alpha]_D$ +52·1° (*c* 0·24 in chloroform), crystallised from light petroleum and was recrystallised from ethyl acetate–light petroleum (Found: 51·0; H, 6·4. $C_8H_{12}O_5$ requires C, 51·1; H, 6·4%).

Acid hydrolysis of methyl 2-O-*acetyl*-3,4-*anhydro*-α-D-*arabinopyranoside*. The acetate (51 mg.) was heated with 80% acetic acid (0·8 ml.) at 100° for 30 min. Evaporation left a colourless syrup which was examined by t.l.c. (ethyl acetate) and by paper chromatography (the paper after irrigation was dried, exposed to ammonia vapour overnight, and then sprayed with periodate and Schiff's reagent [18]). Both methods indicated that the syrup was a mixture of two mono-*O*-acetyl glycosides. The syrup was deacetylated overnight with sodium methoxide in methanol, diluted with water, and sodium ions were removed on a short column of Dowex 50 (NH_4^+) resin. When the evaporated eluate was triturated with ethyl acetate, methyl α-D-lyxopyranoside (28 mg., 63%) crystallised, m. p. 103—104°, $[\alpha]_D$ +52·4° (*c* 1·04 in water), identical with an authentic sample.[19] The mother-liquors were shown by paper chromatography to contain only methyl α-D-lyxopyranoside.

Anhydro-compounds in the β-L-*Series*.—*Methyl* 3,4-*anhydro*-β-L-*arabinopyranoside and* 2,3-*anhydro*-β-L-*lyxopyranoside*. (*a*) Methyl 4-*O*-acetyl-2-*O*-benzoyl-3-*O*-toluene-*p*-sulphonyl-β-L-arabinopyranoside (4·97 g.) was dissolved in methanol (70 ml.) containing sodium methoxide (from 0·79 g. of sodium; *ca.* 3 mol.) and kept at room temperature. After 6 hr., t.l.c. (ethyl acetate) showed the absence of any sulphonyl ester (diphenylamine spray) and that two anhydro-compounds were present (anisaldehyde spray). The solution was neutralised with 2N-sulphuric acid and evaporated to dryness. The residue was extracted with hot benzene (3 × 80 ml.) and the combined extracts were evaporated to a pale yellow syrup. The syrup was dissolved in benzene (100 ml.) and chromatographed on a column of silica gel (45 g.). Benzene–ether (7 : 3) eluted *methyl* 3,4-*anhydro*-β-L-*arabinopyranoside* (0·14 g., 9%), m. p. 32—33° (from ethyl acetate–light petroleum), $[\alpha]_D$ +133° (*c* 0·45 in water) (Found: C, 49·6; H, 6·85. $C_6H_{10}O_4$ requires C, 49·3; H, 6·85%). Benzene–ether (3 : 2) eluted methyl 2,3-anhydro-β-L-lyxopyranoside (0·84 g., 52%), m. p. 65—66° (from ethyl acetate–light petroleum), $[\alpha]_D$ +59·4° (*c* 0·72 in water) (Found: C, 49·4; H, 6·9%). Reist *et al.*[2] give m. p. 70—70·5° (corr.).

(*b*) Methyl 4-*O*-toluene-*p*-sulphonyl-α-D-xyloside (0·20 g.) was dissolved in methanol (5 ml.) containing sodium methoxide (from 44 mg. of sodium; 3·0 mol.) and kept at room temperature for 1½ hr. T.l.c. (ethyl acetate) indicated the presence of one compound (anisaldehyde spray) which was not a sulphonyl ester (diphenylamine spray). The product was isolated as in (*a*), and chromatographed on silica gel (15 g.). Benzene–ether (7 : 3) eluted *methyl* 3,4-*anhydro*-β-L-*arabinopyranoside* (82 mg., 87%), m. p. 31—33°, crystallised from light petroleum. It was indistinguishable from the compound prepared as in (*a*).

Methyl 4-O-*acetyl*-2,3-*anhydro*-β-L-*lyxopyranoside*. The above β-L-anhydrolyxoside (0·65 g.) was acetylated overnight using acetic anhydride (5 ml.) and pyridine (10 ml.). Isolation of the product by means of chloroform yielded the syrupy *acetate* (0·67 g., 76%), $[\alpha]_D$ +81·7° (*c* 2·22 in chloroform) (Found: C, 50·8; H, 6·4. $C_8H_{12}O_5$ requires C, 51·1; H, 6·4%).

Acid hydrolysis of methyl 4-O-*acetyl*-2,3-*anhydro*-β-L-*lyxopyranoside*. The acetate (82 mg.) was heated with 80% acetic acid (1 ml.) at 100° for 20 min. Evaporation left a colourless syrup which was examined by t.l.c. (ethyl acetate) and by paper chromatography. Both methods indicated that the syrupy methyl 4-*O*-acetyl-β-L-arabinopyranoside was homogeneous. It reduced periodate as follows: 0·60 mol. (4 hr.); 0·86 mol. (10 hr.); 0·94 mol. (24 hr.); 0·98 mol. (5 days).

The syrupy acetate (25 mg.) was deacetylated by treatment with sodium methoxide in methanol. The solution was diluted with water, passed through a short column of Dowex 50 (NH_4^+ form) resin, and evaporated to dryness. The crystalline residue recrystallised from ethyl acetate, giving methyl β-L-arabinopyranoside (10 mg., 58%), m. p. 168—170° identical with an authentic sample.

Methyl 4-O-*acetyl*-2,3-*di*-O-*toluene*-p-*sulphonyl*-β-L-*arabinopyranoside*. The above syrupy 4-acetate (50 mg.) was dissolved in pyridine (1 ml.), and toluene-*p*-sulphonyl chloride (160 mg., 3·5 mol.) added with cooling. After 2 days at room temperature the product was isolated by means of chloroform. The disulphonate (68 mg., 54%), m. p. 158—159°, crystallised from light petroleum and was identical with the compound prepared below.

Methyl 2-O-*acetyl*-3,4-*anhydro*-β-L-*arabinopyranoside*. The above β-L-anhydroarabinoside (72 mg.) was acetylated overnight using acetic anhydride (1 ml.) and pyridine (2 ml.). Isolation using chloroform gave *methyl* 2-O-*acetyl*-3,4-*anhydro*-β-L-*arabinopyranoside* (76 mg., 82%), m. p. 49—51° (from ethyl acetate–light petroleum), $[\alpha]_D$ +170° (*c* 0·48 in chloroform) (Found: C, 51·4; H, 6·4. $C_8H_{12}O_5$ requires C, 51·1; H, 6·4%).

Acid hydrolysis of methyl 2-O-*acetyl*-3,4-*anhydro*-β-L-*arabinopyranoside*. The acetate (50 mg.) was heated with 80% acetic acid (2 ml.) at 100° for 35 min. Evaporation left a yellow syrup which was deacetylated with sodium methoxide in methanol. The solution, diluted with water, was passed through a short column of Dowex 50 (NH_4^+ form) resin, and the eluate evaporated to a syrup. When examined by paper chromatography, only methyl β-L-lyxopyranoside could be detected by periodate and Schiff's reagent. Acetylation of the syrup gave methyl 2,3,4-tri-*O*-acetyl-β-L-lyxopyranoside, m. p. 76—78° (from light petroleum). After purification by vacuum-sublimation it had m. p. 84—86° $[\alpha]_D$ +104° (*c* 1·4 in chloroform) (Found: C, 50·0; H, 6·25. $C_{12}H_{18}O_8$ requires C, 49·6; H, 6·2%).

[18] J. Baddiley, J. G. Buchanan, R. Hodges, and J. F. Prescott, *J. Chem. Soc.*, 1957, 4769.

Isbell and Frush [19] report m. p. 88—89° and $[\alpha]_D$ −109·5° (chloroform) for the D-isomer.

Acid Hydrolysis of Methyl 2-O-*Acetyl*-3,4-O-*isopropylidene*-β-L-*arabinoside*.—(*a*) The acetate (0·56 g.) was heated under reflux in methanol (25 ml.) containing 5N-hydrochloric acid (0·5 ml.) for 10 hr.[3] The solution was neutralised (lead carbonate), filtered, and evaporated to dryness. The syrupy residue crystalised from methanol, and was recrystallised from ethanol, to give methyl β-L-arabinopyranoside (0·22 g., 58%), m. p. 168—170°, indistinguishable from an authentic sample.

(*b*) The isopropylidene compound (0·11 g.) was heated with 80% acetic acid (2 ml.) at 100° for 10 min., and the solution evaporated to dryness. The syrupy methyl 2-*O*-acetyl-β-L-arabinopyranoside had $[\alpha]_D$ +197° (*c* 0·91 in chloroform), and reduced 1·25 mol. (constant value) of periodate in 3 days.

Methyl 2-O-*Acetyl*-3,4-*di*-O-*toluene*-p-*sulphonyl*-β-L-*arabinopyranoside*.—The above syrupy 2-acetate (50 mg.) was dissolved in pyridine (3 ml.), and toluene-*p*-sulphonyl chloride (82 mg., 2·1 mol.) added with cooling. After 2 days at room temperature the product was isolated by means of chloroform, to give the *disulphonate* (87 mg., 68%), m. p. 178—179°, $[\alpha]_D$ +149° (*c* 0·32 in chloroform), when recrystallised from ethanol (Found: C, 51·3; H, 5·1. $C_{22}H_{26}O_{10}S_2$ requires C, 51·3; H, 5·1%).

Methyl 4-O-*Acetyl*-2,3-*di*-O-*toluene*-p-*sulphonyl*-β-L-*arabinopyranoside*.— (*a*) Methyl β-L-arabinopyranoside (0·21 g.) was dissolved in pyridine (4 ml.), and toluene-*p*-sulphonyl chloride (0·52 g., 2·1 mol.) was added with cooling. After 5 days at room temperature the product was isolated using chloroform. The resulting syrup was dissolved in benzene and chromatographed on silica gel (20 g.). Benzene–ether (19 : 1) eluted methyl 2,3,4-tri-*O*-toluene-*p*-sulphonyl-β-L-arabinopyranoside (90 mg., 11%), m. p. 110—111°, identical with the compound in (*b*) below. Benzene–ether (9 : 1) eluted a syrupy mixture of three disulphonates (0·43 g., 71%), as shown by t.l.c.; one isomer greatly predominated. The mixture was acetylated overnight with acetic anhydride (4 ml.) and pyridine (8 ml.), and the product isolated with chloroform, to give a syrup which crystallised from light petroleum. Recrystallisation from ethyl acetate–light petroleum afforded the 2,3-*disulphonate* (0·40 g., 85% from the disulphonate mixture), m. p. 159—161°, $[\alpha]_D$ +118° (*c* 0·54 in chloroform) (Found: C, 51·3; H, 5·0. $C_{22}H_{26}O_{10}S_2$ requires C, 51·3; H, 5·1%).

(*b*) Methyl 2-*O*-toluene-*p*-sulphonyl-β-L-arabinopyranoside [3] (2·2 g.) was dissolvd in pyridine (20 ml.), and toluene-*p*-sulphonyl chloride (1·3 g., 1·0 mol.) added with cooling. After 2 days the product was isolated by means of chloroform, to give a syrup which was dissolved in benzene and chromatographed on a column of silica gel (100 g.). Benzene–ether (19 : 1) eluted *methyl tri*-O-*toluene*-p-*sulphonyl*-β-L-*arabinopyranoside* (0·43 g., 10%), m. p. 110—111°, $[\alpha]_D$ +100° (*c* 0·44 in chloroform), which crystallised from ethanol (Found: C, 51·5; H, 4·65. $C_{27}H_{30}O_{11}S_3$ requires C, 51·7; H, 4·8%). Benzene–ether (23 : 2) eluted first a single disulphonate as a syrup which was acetylated overnight with acetic anhydride (2 ml.) and pyridine (4 ml.). Isolation by means of chloroform gave the 2,3-disulphonate (1·21 g., 37%), m. p. 159—161°, identical with the compound prepared in (*a*) above. Continued elution of the column with the same solvent afforded a mixture of two disulphonates; t.l.c. (benzene–ether, 1 : 1) showed that the 2,3-isomer greatly predominated in the mixture.

Treatment of the Anhydropentosides with Alkali.—Qualitative experiments. (*a*) Methyl 2,3-anhydro-α-D-lyxopyranoside (0·65 g.) was dissolved in 0·05M-barium hydroxide solution (95 ml.) and kept at room temperature in a tightly stoppered flask for 5 hr. T.l.c. (ethyl acetate) and measurements of optical rotation indicated that equilibrium had been established. The solution was neutralised (2N-sulphuric acid), the barium sulphate was filtered off, and the filtrate and washings were evaporated to a syrup. The syrup was dissolved in benzene (150 ml.) and chromatographed on a column of silica gel (40 g.). Benzene–ether (17 : 3) eluted starting material (0·14 g., 21%), m. p. 61—62°. Benzene ether (3 : 1) eluted methyl 3,4-anhydro-α-D-arabinopyranoside (0·44 g., 63%), m. p. 94—96°, crystallised from ethyl acetate–light petroleum.

(*b*) Methyl 3,4-anhydro-α-D-arabinopyranoside (69 mg.) was dissolved in 0·05M-barium hydroxide (9·5 ml.), and after 5 hr. the products were isolated as in (*a*). Benzene–ether (17 : 3) eluted methyl 2,3-anhydro-α-D-lyxopyranoside (13 mg., 19%), m. p. 60—62°, crystallised from light petroleum. Benzene–ether (3 : 1) eluted starting material (36 mg., 52%), m. p. 94—96°.

(*c*) Methyl 2,3-anhydro-β-L-lyxopyranoside (195 mg.) was dissolved in 0·05M-barium hydroxide solution (28 ml.), and after 5 hr. the products were isolated as in (*a*). Benzene–ether (4 : 1) eluted methyl 3,4-anhydro-β-L-arabinopyranoside (53 mg., 27%), m. p. 30—32°, after crystallisation from light petroleum. Benzene–ether (7 : 3) eluted starting material (108 mg., 55%), m. p. 64—66°.

(*d*) Methyl 3,4-anhydro-β-L-arabinopyranoside (104 mg.) was dissolved in 0·05M-barium hydroxide solution (14·6 ml.), and after 5 hr. the products were isolated as in (*a*). Benzene–ether (4 : 1) eluted starting material (26 mg., 25%), m. p. 29—31°, crystallised from light petroleum. Benzene–ether (7 : 3) eluted methyl 2,3-anhydro-β-L-lyxopyranoside (59 mg., 57%), m. p. 64—66°, which crystallised from light petroleum.

Polarimetric studies of the epoxide migrations. Each anhydro-compound was dissolved in 0·05M-sodium hydroxide at 25°, and the change in specific rotation with time were measured using a Bendix-Ericsson ETL-NPL Automatic Polarimeter type 143A with a cell of 1 cm. path length. The results are in Table 2.

TABLE 2

Configuration of anhydro-compound	Concn. (mg. ml.$^{-1}$)	$[\alpha]_D$ Initial	$[\alpha]_D$ Final
α-D-Lyxo-	7·55	107·4° (5 min.)	79·9° (7 hr.)
α-D-Arabino- ...	7·00	65·0° (5 min.)	77·4° (5·5 hr.)
β-L-Lyxo-	8·24	61·8° (5 min.)	82·8° (4·5 hr.)
β-L-Arabino- ...	6·00	122·8° (7 min.)	82·8° (3·5 hr.)

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[19] H. S. Isbell and H. L. Frush, *J. Res. Nat. Bur. Stand.*, 1940, **24**, 125.