175. *The Ammonolysis of Methyl 2 : 3-Anhydro-D-furanosides. Part II.* Methyl 2 : 3-Anhydro-5-O-methyl-α- and -β-D-lyxofuranosides.*

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Ammonolyses of methyl 2 : 3-anhydro-5-*O*-methyl-α- and -β-D-lyxofuranosides led to the isolation of crystalline derivatives of methyl 3-amino-3-deoxy-5-*O*-methyl-α- and -β-D-arabinosides. During this work methyl 2-acetamido-2-deoxy-β-D-xylofuranoside, 3-acetamido-3-deoxy-2-*O*-methyl-β-D-arabofuranoside, and 3-acetamido-3-deoxy-2 : 5-*O*-dimethyl-α- and -β-D-arabinosides and two new derivatives of methyl D-xylofuranoside have been prepared.

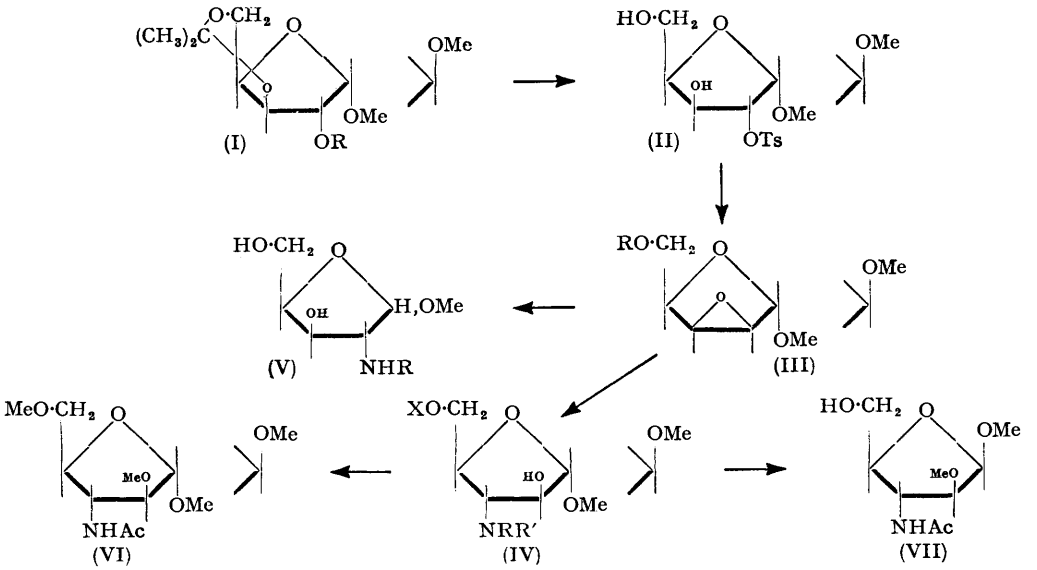
Percival and Zobrist [1] reported the synthesis of methyl 2 : 3-anhydro-α-D-lyxofuranoside (III; R = H) from a mixture of methyl 3 : 5-*O*-*iso*propylidene-α- and -β-D-xylofuranosides (I; R = H) by tosylation (I; R = Ts), mild acid hydrolysis (II), and alkaline hydrolysis of the tosyl residue. Subsequently Baker, Schaub, and Williams,[2] from a similar synthesis, isolated the β-anomer of the 2 : 3-anhydro-sugar (III; R = H), after first partly separating methyl 3 : 5-*O*-*iso*propylidene-αβ-D-xylofuranoside into its two anomers by distillation. Although these authors carried out the subsequent syntheses separately on the two fractions and isolated crystalline methyl 2 : 3-anhydro-α- and -β-D-lyxofuranosides, none of their intermediate derivatives was obtained crystalline. During the present work fractional distillation of the *iso*propylidene-αβ-xylofuranoside led to the separation of two fractions, whose specific rotations differed considerably from the values recorded by Baker and his co-workers. That the present separation was more efficient was confirmed by the ready isolation of the two crystalline methyl 3 : 5-*O*-*iso*propylidene-2-*O*-toluene-*p*-sulphonyl-D-xylofuranosides (I; R = Ts). Hydrolysis of the *iso*propylidene group with boiling

* Part I, Anderson and Percival, *J.*, 1955, 1042.

[1] Percival and Zobrist, *J.*, 1953, 564.

[2] Baker, Schaub, and Williams, *J. Amer. Chem. Soc.*, 1955, **77**, 7.

1% methanolic hydrogen chloride [3] or at 50° with 80% acetic acid [2] caused anomerisation; by use of 0·1% methanolic hydrogen chloride at room temperature, however, no anomerisation occurred and crystalline methyl 2-*O*-toluene-*p*-sulphonyl-α-D-xylofuranoside (II) was obtained in excellent yield.



Crystalline methyl 2 : 3-anhydro-α- [1] and -β-lyxofuranosides [2] were prepared and, after ammonolysis followed by treatment with acetone, gave methyl 3-deoxy-3-*iso*propylideneamino-α- and -β-D-arabofuranosides (IV; RR′ = CMe_2, X = H), respectively. The mother liquors were examined for methyl 2-amino-2-deoxyxylofuranoside (V; R = H) derivatives. The *N*-acetyl-3 : 5-*iso*propylidene derivative appeared to be the most appropriate to prepare, but specific *N*-acetylation and attempted condensation with acetone failed to yield any crystalline derivatives from the mother liquors of the α-anomer. The mother liquors of the β-anomer, however, gave crystals (0·6% of the ammonolysis product) which gave correct analytical results for a methyl 2-acetamido-2-deoxyxylofuranoside (V; R = Ac) and were converted into a free sugar hydrochloride whose rotation was identical with that recorded [4] for 2-amino-2-deoxy-D-xylose hydrochloride.

Methylation of both anomers of methyl 3-acetamido-3-deoxy-D-arabofuranoside [5] (IV; R = H, R′ = Ac, X = H) gave the respective crystalline 2 : 5-dimethyl ethers (VI). Complete methylation proved difficult in the β-series; after three treatments two crops of crystals were obtained. The first was shown by chromatography to be a single entity and by analysis to be a methyl 3-acetamido-3-deoxymonomethylarabinoside. Determination of melting point of mixtures showed that it was not the 5-methyl ether, and conversion into a toluene-*p*-sulphonate which showed the presence of a primary toluene-*p*-sulphonyloxy-group [6] proved it to be methyl 3-acetamido-3-deoxy-2-*O*-methyl-β-D-arabofuranoside (VII). The second crop of crystals was shown by paper chromatography and by analysis to be a mixture of mono- and di-methyl ethers. Three further methylations of the mother liquors were necessary before the pure dimethyl ether (VI) could be isolated.

Methylation of both anomers of methyl 2 : 3-anhydro-D-lyxofuranoside (III; R = H) gave crystalline α- and β-5-methyl ethers (III; R = Me) which on ammonolysis and appropriate treatment gave crystalline *N-iso*propylidene and *N*-acetyl derivatives. That these were derivatives of 3-amino-3-deoxy-D-arabinose was proved by the isolation, after

[3] Percival and Zobrist, *J.*, 1952, 4306.
[4] Wolfrom and Anno, *J. Amer. Chem. Soc.*, 1953, **75**, 1038.
[5] Anderson and Percival, *J.*, 1955, 1042.
[6] Tipson, Clapp, and Cretcher, *J. Org. Chem.*, 1947, **12**, 133.

complete methylation, of crystalline dimethyl ethers identical with the 2 : 5-dimethyl ethers (VI) obtained above. No crystalline derivatives of xylose could be isolated from the mother liquors after the removal of the *N-iso*propylidene (α-5-methyl) and *N*-acetyl (β-5-methyl) arabinose derivatives.

Although Baker and his co-workers [2] record sharp melting points and correct analyses for the *N-iso*propylidene derivatives, we were unable, even after repeated recrystallisation, to isolate crystals of pure methyl 3-deoxy-3-*iso*propylideneamino-α- or -β-arabofuranosides (IV; RR′ = CMe_2, X = H) or of the corresponding α-5-methyl ether (IV; R_2 = CMe_2, X = Me). It is thought that the extreme acid-lability of the *iso*propylidene group probably leads to contamination with the amino-sugar.

Cleavage of the epoxide ring in methyl 2 : 3-anhydrolyxofuranosides (III) with ammonia can yield, in theory, 3-amino-3-deoxyarabinose (IV) and 2-amino-2-deoxyxylose (V) derivatives, depending on whether the break occurs between $C_{(3)}$ or $C_{(2)}$ and the oxygen of the ring. In all the derivatives studied, only a very small quantity of a xylose derivative was isolated in a single experiment. Fission of the epoxide ring with ammonia occurred preferentially between $C_{(3)}$ and the attached oxygen atom, the attacking group entering at $C_{(3)}$, since 3-amino-3-deoxyarabinose derivatives were isolated in every experiment. No attempt will be made to explain the reason for this preferential cleavage or the mechanism of fission until work on other epoxide derivatives of furanose sugars has been carried out.

Experimental

Solvents were removed under reduced pressure. Methanolic ammonia was prepared by saturating dry methanol with ammonia at 0°. Light petroleum was the fraction, b. p. 60—80°. The solvent used in chromatographic separation on Whatman No. 1 paper was butanol–ethanol–water (4 : 1 : 5). Chlorine and starch–potassium iodide [7] were used as detecting agent for the amino-compounds. The R_G values were assessed by using tetramethylglucose (R_G 1·0) as standard.

Methyl 3 : 5-O-iso*Propylidene*-2-O-*toluene*-p-*sulphonyl*-α- *and* -β-D-*xylofuranoside*.—Methyl 3 : 5-*O-iso*propylidene-D-xylofuranoside was prepared from D-xylose [1] (200 g.); the crude product was purified by chloroform extraction (3 × 200 ml.) of an aqueous solution (200 ml.). Repeated fractional distillation (fractions of similar specific rotation were combined and refractionated) of the concentrated chloroform extracts (172 g.; in 30 g. portions) through a Vigreux column led finally to the separation of two fractions. Fraction I: 71·6 g. (42%), b. p. 60—70°/0·05 mm., $[\alpha]_D$ +75° (*c*, 1·0 in $CHCl_3$; average: range, +70°—+82°), n_D^{18} 1·4683. Fraction II: 55·2 g. (32%), b. p. 90—100°/0·05 mm., $[\alpha]_D$ −80° (*c*, 1·0 in $CHCl_3$; average: range, −65° to −85°), n_D^{17} 1·4650. Baker *et al.*[2] record for fraction I, $[\alpha]_D^{24}$ +18° in H_2O, and for fraction II, $[\alpha]_D^{24}$ −64° in H_2O.

Methyl 3 : 5-*O-iso*propylidene-D-xylofuranoside (71 g.; $[\alpha]_D$ +75°) was treated in pyridine (120 ml.) with toluene-*p*-sulphonyl chloride (73 g.).[8] A crystalline product (92 g., 74%), m. p. 77°, $[\alpha]_D^{21}$ +66° (*c*, 1·4 in $CHCl_3$), was isolated. After recrystallisation from light petroleum, *methyl* 3 : 5-O-iso*propylidene*-2-O-*toluene*-p-*sulphonyl*-α-D-*xylofuranoside* (I; R = Ts) had m. p. 79—80°, $[\alpha]_D^{18}$ +68° (*c*, 1·1 in $CHCl_3$) (Found: C, 53·2; H, 6·1; S, 8·9. $C_{16}H_{22}O_7S$ requires C, 53·2; H, 6·2; S, 9·0%).

Methyl 3 : 5-*O-iso*propylidene-D-xylofuranoside (55 g.; $[\alpha]_D$ −80°) after similar treatment gave a product (80 g.), $[\alpha]_D^{18}$ −37° (*c*, 1·1 in $CHCl_3$). Recrystallisation from aqueous methanol gave methyl 3 : 5-*O-iso*propylidene-2-*O*-toluene-*p*-sulphonyl-β-D-xylofuranoside (I; R = Ts) (62 g., 64%), m. p. 119—120°, $[\alpha]_D^{17}$ −53° (*c*, 0·9 in $CHCl_3$), $[\alpha]_D^{18}$ −44° (*c*, 0·4 in MeOH). This was identical with the material isolated by Percival and Zobrist [3] from syrupy methyl 3 : 5-*O-iso*propylidene-αβ-D-xylofuranoside.

Methyl 2-O-*Toluene*-p-*sulphonyl*-α- *and* -β-D-*xylofuranosides*.—Methyl 3 : 5-*O-iso*propylidene-2-*O*-toluene-*p*-sulphonyl-α-D-xylofuranoside (89 g.), dissolved in 0·1% methanolic hydrogen chloride (20 ml.), was kept at room temperature until the rotation reached a constant value: α_D +1·46° (initial), +1·95° (5 min.), +2·12 (15 min.), +2·13 (20 min.; const.). After neutralisation with silver carbonate, a syrup (75 g., 95%) was obtained which crystallised completely. Recrystallisation from chloroform–light petroleum gave *methyl* 2-O-*toluene*-p-*sulphonyl*-α-D-*xylofuranoside* (II), m. p. 90—91°, $[\alpha]_D^{25}$ +101° (*c*, 1·3 in $CHCl_3$) (Found: C, 49·5;

[7] Rydon and Smith, *Nature*, 1952, **169**, 922.
[8] Edington, Hirst, and Percival, *J.*, 1955, 2281.

H, 5·8; S, 10·4. $C_{13}H_{18}O_7S$ requires C, 49·1; H, 5·7; S, 10·1%). The β-form was isolated as a syrup (95%), $[\alpha]_D^{22}$ −20° (*c*, 1·0 in $CHCl_3$), n_D^{23} 1·5243.

Attempted Isolation of Xylose Derivatives.—Ammonolysis of methyl 2 : 3-anhydro-α-D-lyxofuranoside (III; R = H) (13·2 g.) by heating it with methanolic ammonia in an autoclave at 120° for 48 hr. gave, after treatment with charcoal, a brown syrup (14·6 g., 99%). This was dissolved in hot acetone (250 ml.);[2] the cooled solution deposited methyl 3-deoxy-3-*iso*propylideneamino-α-D-arabofuranoside (IV; $R_2 = CMe_2$, X = H). The total yield, after several treatments of the mother liquors, was 15·5 g. (85%). *N*-Acetylation of the residual material (1·8 g., 10%) in water (50 ml.) with methanol (5 ml.), resin (50 ml.), and acetic anhydride (1·25 ml.)[9] gave a syrup (1·5 g., 83%). When shaken with acetone (50 ml.), anhydrous copper sulphate (8 g.), and N-sulphuric acid (0·08 ml.),[2] and then treated appropriately, this yielded a non-reducing syrup (1·0 g.). Fractionation of this between chloroform and water by a counter-current technique gave, from the aqueous fraction, a non-reducing syrup (900 mg., 90%), $[\alpha]_D^{22}$ +112° (*c*, 1·1 in H_2O), which gave a negative iodoform test for the *iso*propylidene group. Paper chromatography showed the presence of two components, having R_G 0·67 and 0·76 (methyl 3-acetamido-3-deoxy-α-D-arabofuranoside has R_G 0·73). The chloroform fraction yielded a non-reducing syrup (40 mg., 4%), which was not examined further.

Methyl 2 : 3-anhydro-β-D-lyxofuranoside (III; R = H) (8·4 g.) gave, after ammonolysis and appropriate treatment, methyl 3-deoxy-3-*iso*propylideneamino-β-D-arabofuranoside (IV; RR′ = CMe_2, X = H) (7·1 g., 62%). The residue (3·5 g.) was *N*-acetylated[9] and the syrupy product (3·4 g., 96%) condensed with dry acetone[2] as above, giving a non-reducing syrup (3·0 g.), $[\alpha]_D^{22}$ −48° (*c*, 1·5 in H_2O), which was fractionated between chloroform and water. The aqueous fraction gave a non-reducing syrup (2·65 g., 88·5%) which after distillation at 170—175°/0·1 mm. (0·94 g.) showed on chromatographic analysis spots with R_G 0·60 and 0·70 (methyl 3-acetamido-3-deoxy-β-D-arabofuranoside has R_G 0·65). A solution of this syrup in ethanol–light petroleum deposited crystals (60 mg.), m. p. 222—224°, $[\alpha]_D^{26}$ −64° (*c*, 0·9 in H_2O), R_G 0·60 (Found: C, 46·4; H, 7·4. $C_8H_{15}O_5N$ requires C, 46·8; H, 7·4%). A solution of the crystals (13·5 mg.) in hydrochloric acid (10 ml.; 3N) was heated at 100° for 30 min. Concentration to dryness gave a syrup (12·2 mg.) which crystallised; the solid had $[\alpha]_D^{18}$ +40° (*c*, 0·60 in H_2O) (Wolfrom and Anno[4] record $[\alpha]_D$ +40° for 2-amino-2-deoxy-D-xylose hydrochloride).

The chloroform fraction yielded a dark brown syrup (70 mg., 2·3%) which was not examined further.

Methyl 3-Acetamido-3-deoxy-2 : 5-di-O-methyl-α- and -β-D-arabofuranosides.—Methyl 3-acetamido-3-deoxy-α-D-arabofuranoside[5] (IV; R = H, R′ = Ac, X = H) (4·0 g.) was methylated four times with methyl iodide (23 ml.) and silver oxide (20 g.). The product, a mobile syrup (4·30 g.), after distillation at 50—120°/0·05 mm., had n_D^{20} 1·4647. This partly crystallised; the hygroscopic crystals (2·69 g., 59%) of *methyl 3-acetamido-3-deoxy-2 : 5-di-O-methyl-α-D-arabofuranoside* (VI) could not be recrystallised. Freed from syrup by cold light petroleum they had m. p. 57—59°, $[\alpha]_D^{23}$ +131° (*c*, 1·0 in H_2O), R_G 0·97 (Found: C, 51·6; H, 8·1; N, 5·8; OMe, 39·2. $C_{10}H_{19}O_5N$ requires C, 51·5; H, 8·2; N, 6·0; OMe, 39·9%).

Methyl 3-acetamido-3-deoxy-β-D-arabofuranoside[5] (IV; R = H, R′ = Ac, X = H) (2·0 g.) in methanol (15 ml.) after three methylations with Purdie's reagents gave a product (0·90 g.), which was dissolved in acetone. Cooling the solution gave crystals *A* (580 mg.). Addition of light petroleum caused the deposition crystals *B* (280 mg.). Crystals *A* were non-reducing and after recrystallisation (acetone) depressed the m. p. of the starting material, crystals *B*, and methyl 3-acetamido-3-deoxy-5-*O*-methyl-β-D-arabofuranoside. The crystals, m. p. 157°, were therefore *methyl 3-acetamido-3-deoxy-2-O-methyl-β-D-arabofuranoside*, $[\alpha]_D^{24}$ −118° (*c*, 0·7 in H_2O), R_G 0·77 (Found: C, 49·7; H, 7·9; N, 6·3; OMe, 28·3. $C_9H_{17}O_5N$ requires C, 49·3; H, 7·8; N, 6·4; OMe, 28·3%). Tosylation[8] (50 mg.) gave a crystalline toluene-*p*-sulphonate (55 mg.), m. p. 85—86°, $[\alpha]_D^{22}$ −69° (*c*, 0·9 in $CHCl_3$), which gave a positive test for a primary toluene-*p*-sulphonyloxy-group.[6]

Crystals *B* were also non-reducing, and after recrystallisation (acetone–light petroleum) had m. p. 156—160° (Found: C, 51·0; H, 8·5; N, 5·0; OMe, 36·2. $C_{10}H_{19}O_5N$ requires C, 51·5; H, 8·2; N, 6·0; OMe, 39·9%). The m. p.s of starting material, crystals *A*, and methyl 3-acetamido-3-deoxy-5-*O*-methyl-β-D-arabofuranoside were all depressed. Chromatographic analysis showed two spots, R_G 0·92 and R_G 0·78.

The residue (1·1 g.; OMe, 24·9%) left after the separation of crystals *A* and *B* was thrice methylated with Purdie's reagents. The product (1·0 g.; OMe, 36·5%) was extracted with

[9] Roseman and Ludowieg, *J. Amer. Chem. Soc.*, 1954, **76**, 301.

cold acetone (2 ml.). Addition of light petroleum gave needles of *methyl* 3-*acetamido*-3-*deoxy*-2 : 5-*di*-O-*methyl*-β-D-*arabofuranoside* (VI) (0·51 g.) which after recrystallisation had m. p. 174—175°, $[\alpha]_D^{23}$ −107° (*c*, 0·8 in H_2O), R_G 0·92 (Found: C, 51·6; H, 8·1; N, 5·9; OMe, 39·4. $C_{10}H_{19}O_5N$ requires C, 51·5; H, 8·2; N, 6·0; OMe, 39·9%).

Methyl 2 : 3-*Anhydro*-5-*methyl*-β-D-*lyxofuranoside*.—Methyl 2 : 3-anhydro-β-D-lyxofuranoside [2] (III; R = H) (8·0 g.), initially dissolved in dry methanol (15 ml.), was thrice methylated with Purdie's reagents. The product (7·3 g.), a very mobile syrup, $[\alpha]_D^{26}$ −84° (*c*, 0·7 in H_2O), gave on distillation (b. p. 54—57°/0·05 mm.) a syrup (6·4 g., 73%) which crystallised when cooled to 0° but melted at *ca.* 14—15°. It had $[\alpha]_D^{20}$ −88° (*c*, 1·1 in H_2O), n_D^{21} 1·4470 (Found: C, 52·8; H, 7·8; OMe, 39·1. $C_7H_{12}O_4$ requires C, 52·5; H, 7·6; OMe, 38·8%).

Ammonolysis of Methyl 2 : 3-*Anhydro*-5-O-*methyl*-α-D-*lyxofuranoside*.—A solution of methyl 2 : 3-anhydro-5-*O*-methyl-α-D-lyxofuranoside [1] (III; R = Me) (9·1 g.) in dry methanolic ammonia (500 ml.) was heated in an autoclave at 120° for 48 hr. The resulting brown syrup after filtration and treatment with charcoal was concentrated, and the product freed from ammonia by distillation with ethanol. The residue, a brown syrup (9·51 g., 94%), was dissolved in hot acetone and the solution cooled. Crystals (8·34 g., 72%), shown to be *methyl* 3-*deoxy*-5-O-*methyl*-3-iso*propylideneamino*-α-D-*arabofuranoside* (IV; RR′ = CMe_2, X = Me), were deposited and after several recrystallisations (acetone) had m. p. 115—125°, $[\alpha]_D^{22}$ +106° (*c*, 0·9 in H_2O) (Found: C, 54·3; H, 9·4; N, 6·4. $C_{10}H_{19}O_4N$ requires C, 55·3; H, 8·8; N, 6·5%). Concentration of the mother liquors gave a dark brown syrup (2·82 g.), $[\alpha]_D$ +65° (*c*, 0·7 in H_2O). Distillation at 100° (bath temp.)/0·03 mm. gave a syrup (520 mg.) from which more (80 mg.) of the crystals were isolated.

The crystalline *N-iso*propylidene derivative (5·81 g.) in water (150 ml.) was acidified with 2N-hydrochloric acid and *N*-acetylated.[9] The syrupy product (5·80 g., 99%) crystallised after distillation at 140°/0·05 mm. All attempts at recrystallisation failed; the hygroscopic *methyl* 3-*acetamido*-3-*deoxy*-5-O-*methyl*-α-D-*arabofuranoside* (3·87 g.) (IV; R = H, R′ = Ac, X = Me), freed from syrup by ether, had m. p. 60—62°, $[\alpha]_D^{21}$ +119° (*c*, 0·9 in H_2O), R_G 0·88 (Found: C, 48·2; H, 7·6; N, 5·9; OMe, 27·8. $C_9H_{17}O_5N$ requires C, 49·3; H, 7·8; N, 6·4; OMe, 28·3%).

Four methylations with Purdie's reagents gave a mobile syrup (1·07 g. from 1·0 g.), n_D^{22} 1·4548. Distillation gave two fractions: (*a*) 310 mg., b. p. (bath temp.) 80°/0·02 mm., which was not examined further; and (*b*) 520 mg., b. p. 100°/0·02 mm., which crystallised. Recrystallisation was difficult but the crystals were freed from syrup with light petroleum. They had m. p. and mixed m. p. 57—59° with authentic methyl 3-acetamido-3-deoxy-2 : 5-di-*O*-methyl-α-D-arabofuranoside (VI), $[\alpha]_D$ +129° (*c*, 0·9 in H_2O), R_G 0·97 (Found: OMe, 39·1. Calc. for $C_{10}H_{19}O_5N$: OMe, 39·9%).

Ammonolysis of Methyl 2 : 3-*Anhydro*-5-O-*methyl*-β-D-*lyxofuranoside*.—A brown syrup (6·17 g., 90%) was obtained when methyl 2 : 3-anhdyro-5-*O*-methyl-β-D-lyxofuranoside (III; R = Me) (6·2 g.) was treated with methanolic ammonia (500 ml.) under the conditions used for the α-anomer. Attempts to prepare an *N-iso*propylidene [2] derivative gave, after distillation at 84—86°/0·03 mm., a syrup (5·64 g., 74%). *N*-Acetylation [8] gave a syrup (5·44 g., 96%) which on dissolution in acetone and addition of light petroleum deposited crystals (2·66 g., 48%), shown to be *methyl* 3-*acetamido*-3-*deoxy*-5-O-*methyl*-β-D-*arabofuranoside* (IV; R_2 = H, R′ = Ac, X = Me), m. p. 161—162° after recrystallisation (acetone–light petroleum), $[\alpha]_D^{23}$ −114° (*c*, 1·2 in H_2O), R_G 0·81 (Found: C, 49·5; H, 7·8; N, 5·8; OMe, 28·1. $C_9H_{17}O_5N$ requires C, 49·3; H, 7·8; N, 6·4; OMe, 28·3%).

Evaporation of the mother liquors and distillation gave a syrup (71 mg.), $[\alpha]_D^{20}$ +30° (*c*, 0·7 in H_2O). An aqueous extract of the distillation residues yielded another syrup (80 mg.), $[\alpha]_D^{23}$ +18° (*c*, 0·8 in H_2O).

Methyl 3-acetamido-3-deoxy-5-*O*-methyl-β-D-arabofuranoside (IV; R = H, R′ = Ac, X = Me) (1·0 g.) in methanol (5 ml.) was methylated four times with Purdie's reagents. The product (1·0 g.) was dissolved in acetone and light petroleum added, giving methyl 3-acetamido-3-deoxy-2 : 5-di-*O*-methyl-β-D-arabofuranoside (VI) identical with that synthesised as above. The samples had m. p. and mixed m. p. with authentic material 174—175°, $[\alpha]_D^{23}$ −107° (*c*, 1·1 in H_2O), R_G 0·92 (Found: OMe, 40·1. Calc. for $C_{10}H_{19}O_5N$: OMe, 39·9%.

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