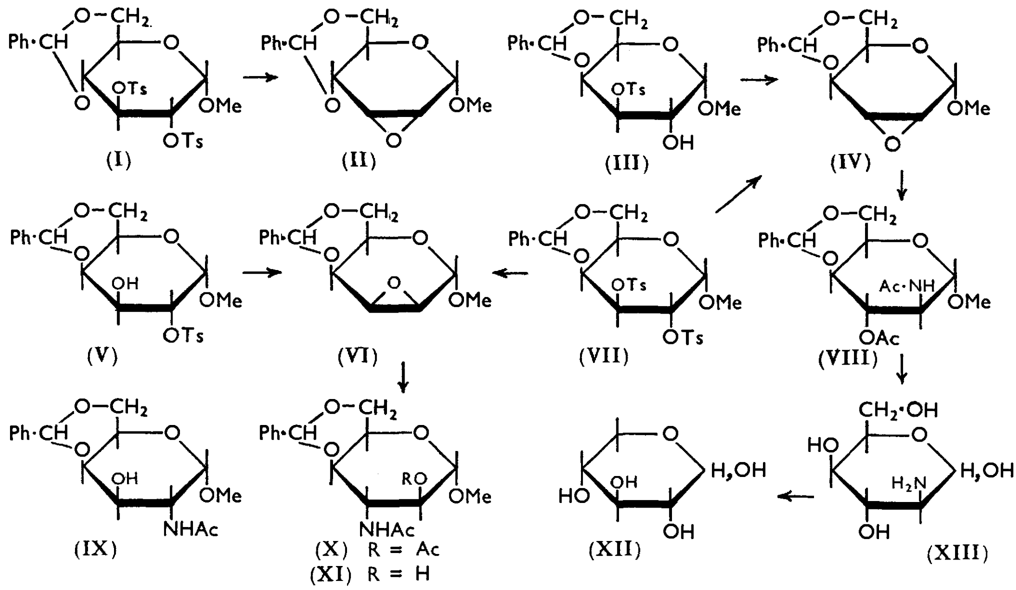
677. *The Action of Ammonia on Methyl 2,3-Anhydro-4,6-O-Benzylidene-α-D-Guloside and -Taloside.*

By J. G. Buchanan and K. J. Miller.

With aqueous ammonia methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-guloside and -taloside give predominantly products of the idose configuration.

METHYL 2,3-ANHYDRO-4,6-*O*-BENZYLIDENE-α-D-GULOSIDE (IV) and -α-D-taloside (VI) were first adequately characterised by Sorkin and Reichstein,[1] who prepared them from the corresponding monotoluene-*p*-sulphonates (III) and (V). Reber and Reichstein [2] found that treatment of the ditoluene-*p*-sulphonate (VII) with sodium methoxide gave a mixture of anhydroguloside (IV) and anhydrotaloside (VI), correcting the earlier statement [1] that the anhydroguloside (IV) was the sole product of this reaction. The behaviour of the disulphonate (VII) is in contrast to that of the corresponding glucose compound (I) from which only one anhydro-compound, the anhydroalloside (II), is formed.[3]



In 1943, Myers and Robertson [4] described the reaction of " 4,6-benzylidene-2,3-anhydro-α-methylguloside (or taloside) " with ammonia. The preparation of the initial

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[1] Sorkin and Reichstein, *Helv. Chim. Acta*, 1945, **28**, 1.

[2] Reber and Reichstein, *Helv. Chim. Acta*, 1945, **28**, 1164.

[3] Robertson and Griffith, *J.*, 1935, 1193; Richtmyer and Hudson, *J. Amer. Chem. Soc.*, 1941, **63**, 1727.

[4] Myers and Robertson, *J. Amer. Chem. Soc.*, 1943, **65**, 8.

anhydro-compound was not published,[4,5] and it seemed likely that it had been made from the galactoside disulphonate and was therefore a mixture of anhydro-guloside and -taloside. Such mixtures are highly crystalline [1] and we have found them not to be resolvable by recrystallisation. As part of another investigation [6] we had available authentic samples of each anhydro-compound and we have repeated Myers and Robertson's work.

Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-guloside (IV) was treated with concentrated aqueous ammonia at 120° for 48 hr. The product was converted into a diacetyl derivative, in 80% yield, having m. p. 185° and $[\alpha]_D$ +45·7°, clearly the "3(or 2)-acetyl-4,6-benzylidene-2(or 3)acetamido-α-methylidoside" of m. p. 188° and $[\alpha]_D$ +43·4° isolated by Myers and Robertson [4] as their major product. This could be a derivative either of 3-amino-3-deoxygalactose or of 2-amino-2-deoxyidose. That it was the latter was shown by acid-hydrolysis followed by ninhydrin oxidation,[7] which gave a pentose identified chromatographically as xylose. The diacetyl compound is therefore methyl 2-acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-α-D-idoside (VIII), giving 2-amino-2-deoxy-D-idose (XIII) and xylose (XII) on degradation.

When the anhydrotaloside (VI) was treated similarly, a diacetyl derivative was isolated, in 73% yield, with m. p. 289—290° and $[\alpha]_D$ +84·4°, corresponding to Myers and Robertson's "3(or 2)-acetyl-4,6-benzylidene-2(or 3)-acetamido-α-methyl galactoside," m. p. 260°, $[\alpha]_D$ +70·3°. De-*O*-acetylation of this compound gave the *N*-acetyl derivative, m. p. 226°, $[\alpha]_D$ +47·7°. These constants differ from those of methyl *N*-acetyl-4,6-*O*-benzylidene-α-D-galactosaminide [8] (IX), m. p. 243—245°, $[\alpha]_D$ +149°, one of the possible products of this reaction. The *ON*-diacetyl compound is therefore methyl 3-acetamido-2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-α-D-idoside (X), giving the monoacetyl compound (XI).

The formation of idose derivatives by the reaction of both anhydro-sugars with ammonia agrees with other work on the action of hydroxide and methoxide ion on these compounds; [1] it represents diaxial opening of the oxides [9] if the latter are considered to be in the "O-inside" conformation.[10] Since we have not isolated any galactoside isomers, it is probable that Myers and Robertson were dealing with a mixture of anhydro-sugars.

When this work was nearing completion, we heard from Dr. R. W. Jeanloz that he also had re-investigated Myers and Robertson's work and had reached the same conclusions. We thank him for informing us of his work before its publication.

EXPERIMENTAL

Infrared spectra were measured for KBr discs.

Methyl 2-Acetamido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-α-D-idoside (VIII).—Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-guloside (0·4 g.) was heated with aqueous ammonia (*d* 0·88; 10 c.c.) at 120° for 48 hr. The solution was evaporated to a syrup, which was dissolved in chloroform and dried (Na_2SO_4). The chloroform solution was evaporated and the residue treated with acetic anhydride (5 c.c.) in pyridine (10 c.c.) for 48 hr. Isolated by use of chloroform the diacetyl compound (0·5 g., 80%) had m. p. 181°. After recrystallisation from ethanol it had m. p. 185°, $[\alpha]_D^{26}$ +45·7° (*c* 1·06 in $CHCl_3$) (Found: C, 59·4; H, 6·7. Calc. for $C_{18}H_{23}O_7N$: C, 59·2; H, 6·3%), $\nu_{max.}$ 1739 (ester C=O) and 1656 cm.$^{-1}$ (amide C=O).

Formation of Xylose by Ninhydrin Oxidation.—The above compound (5 mg.) was heated with N-hydrochloric acid (0·5 c.c.) in a sealed tube at 100° for 48 hr. After evaporation the residue was treated with ninhydrin in aqueous pyridine [7] at 100° for 30 min., and the product chromatographed on Whatman No. 4 paper in butan-1-ol–ethanol–water (4 : 1 : 1 v/v). After

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[5] Robertson, Myers, and Tetlow, *Nature*, 1938, **142**, 1076; Robertson and Myers, *Nature*, 1939, **143**, 640.

[6] Buchanan, *J.*, 1958, 995.

[7] Stoffyn and Jeanloz, *Arch. Biochem. Biophys.*, 1954, **52**, 373.

[8] Stoffyn and Jeanloz, *J. Amer. Chem. Soc.*, 1954, **76**, 561.

[9] Newth, *Quart. Rev.*, 1959, **13**, 30.

[10] Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 43.

spraying with aniline phthalate,[11] a single pentose spot of R_{Ribose} 0·86 appeared. On the same chromatogram known pentoses had the following R_{Ribose} values: xylose, 0·86; lyxose (from ninhydrin oxidation of galactosamine, 0·96; arabinose, 0·77.

Methyl 3-*Acetamido*-2-O-*acetyl*-4,6-O-*benzylidene*-3-*deoxy*-α-D-*idoside* (X).—The anhydrotaloside (VI) (0·4 g.) was heated with ammonia (*d* 0·88; 10 c.c.) at 120° for 48 hr. The solution was evaporated to a white solid (0·4 g.; m. p. 137—138°) which with pyridine (10 c.c.) and acetic anhydride (2 c.c.) (48 hr. at room temperature) gave the diacetyl derivative (0·4 g., 73%), m. p. 282—284° (decomp.) Recrystallised from ethanol it had m. p. 289—290° (decomp.), $[\alpha]_D^{23}$ +84·4° (*c* 1·25 in $CHCl_3$) (Found: C, 58·9; H, 6·4. Calc. for $C_{18}H_{23}O_7N$: C, 59·2; H, 6·3%), $\nu_{\text{max.}}$ 1740 (ester C=O) and 1670 cm.$^{-1}$ (amide C=O).

Methyl 3-*Acetamido*-4,6-O-*benzylidene*-3-*deoxy*-α-D-*idoside* (XI).—The preceding diacetyl compound (0·2 g.) was left in methanol (20 c.c.) containing sodium methoxide (from 0·02 g. of sodium) for 24 hr. at room temperature. Some diacetyl compound remained undissolved and the mixture was warmed to give a clear solution and left for a further 20 hr. at room temperature. The N-*acetyl compound*, which had crystallised, was filtered off [needles (0·12 g., 67%), m. p. 220°]. Recrystallised from ethanol it had m. p. 226°, $[\alpha]_D^{24}$ +47·0° (*c* 0·98 in $CHCl_3$) (Found: C, 59·0; H, 6·5. $C_{16}H_{21}O_6N$ requires C, 59·5; H, 6·5%), $\nu_{\text{max.}}$ 1628 cm.$^{-1}$ (amide C=O) (shoulder at 1648 cm.$^{-1}$) but no ester-carbonyl band.

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[11] Partridge, *Nature*, 1949, **164**, 443.