288. *Derivatives of 3-Acetamido-3-deoxy-D-altrose and Their Conversion into 2-Acetamido-2-deoxy-D-ribose.**

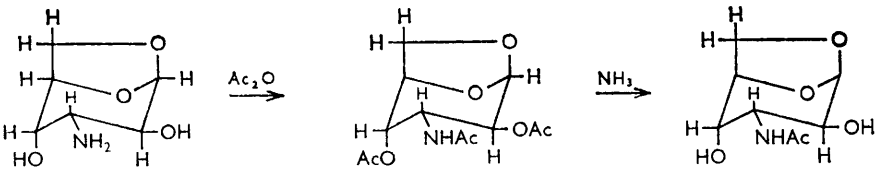
By Bruce Coxon and L. Hough.

3-Acetamido-3-deoxy-D-altrose has been prepared from 3-amino-1,6-anhydro-3-deoxy-β-D-altropyranose, and its periodate oxidation investigated. This hexose derivative was not oxidized to any large extent in the pyranose form.

Oxidation of the diethyl dithioacetal of 3-acetamido-3-deoxy-D-altrose with peroxypropionic acid gave a mixture of (2-acetamido-2-deoxy-β-D-ribopyranosyl)diethylsulphonylmethane and 2-acetamido-2-deoxy-D-ribose.

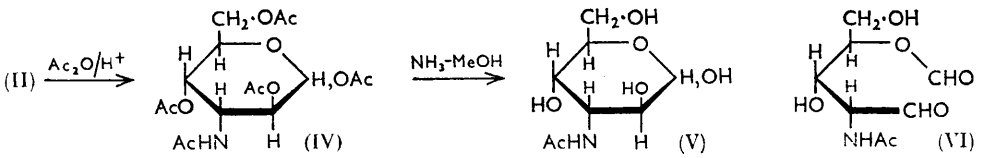
Current biochemical interest in amino-sugars prompted an investigation of the synthesis of 2-acetamido-2-deoxy-D-ribose (XV) by removal of $C_{(1)}$ from derivatives of 3-acetamido-3-deoxy-D-altrose which are readily synthesized from D-glucose.

Hydrolysis of methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside [1,2] with hydrochloric acid gave the hydrochloride of 3-amino-1,6-anhydro-3-deoxy-β-D-altropyranose (I) which was presumably formed through 3-amino-3-deoxy-D-altrose. This



(I) (II) (III)

anhydro-compound (previously named "anhydroepiglucosamine" [3]) was presumed [2] to be a 1,6-anhydro-derivative by analogy with 1,6-anhydro-β-D-altropyranose. Acetylation gave 3-acetamido-2,4-di-*O*-acetyl-1,6-anhydro-3-deoxy-β-D-altropyranose (II) which, on de-*O*-acetylation in methanolic ammonia, yielded 3-acetamido-1,6-anhydro-3-deoxy-β-D-altropyranose (III). In agreement with the 1,6-anhydro-structure, the last derivative did not consume periodate, whereas the parent 3-amino-3-deoxy-derivative (I) consumed



two mol. of periodate and gave one mol. of titratable acid. Similar results were obtained for 2-amino-1,6-anhydro-2-deoxy-β-D-altropyranose by Foster, Stacey, and Vardheim.[4] The triacetyl derivative (II) was remarkably soluble in water as a result of the hydrophilic nature of the acetamido-group, which apparently counteracts the hydrophobic properties of the acetoxy-group. Fischer and Richardson [5] tell us that 3-acetamido-2,4-di-*O*-acetyl-1,6-anhydro-3-deoxy-β-D-gulopyranose is also soluble in water.

Acetolysis [6] of the triacetyl derivative (II) with sulphuric or perchloric acid [7] as catalyst

* For a preliminary account of this work see Coxon and Hough, *Chem. and Ind.*, 1959, 1249.

[1] Robertson, Myers, and Tetlow, *Nature*, 1938, **142**, 1076; Myers and Robertson, *J. Amer. Chem. Soc.*, 1943, **65**, 8; Baker and Schaub, *J. Org. Chem.*, 1954, 646.

[2] Wiggins, *J.*, 1947, 18.

[3] Levene and Meyer, *J. Biol. Chem.*, 1923, **55**, 221.

[4] Foster, Stacey, and Vardheim, *Acta Chem. Scand.*, 1958, **12**, 1605.

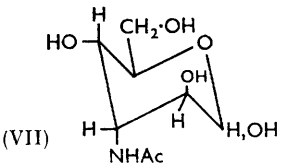
[5] Fischer and Richardson, personal communication.

[6] Richtmyer and Hudson, *J. Amer. Chem. Soc.*, 1941, **63**, 1727.

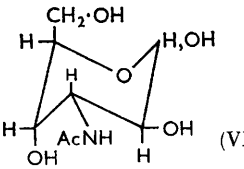
[7] Bredereck, Wagner, Hagelloch, and Faber, *Chem. Ber.*, 1958, **91**, 515; Richtmyer and Pratt, *J. Amer. Chem. Soc.*, 1956, **78**, 4717.

gave 3-acetamido-1,2,4,6-tetra-*O*-acetyl-3-deoxy-αβ-D-altropyranoses (IV). Methanolic ammonia rather slowly (*ca.* 24 hr.) deacetylated this to 3-acetamido-3-deoxy-D-altrose (V) which crystallized after paper chromatography or fractional elution from charcoal.[8]

Periodate oxidation of 3-acetamido-3-deoxy-D-altrose was examined at pH 3·7,[9] since reaction in the pyranose form (V) with 1 mol. of periodate would have given 2-acetamido-2-deoxy-4-*O*-formyl-D-ribose (VI). Formyl esters of this type are usually [9] stable to periodate under these conditions of pH. However, a mutarotated solution of 3-acetamido-3-deoxy-D-altrose (V) at pH 3·7 reacted quickly (1 hr.) with two mol. of periodate and then slowly (24 hr.) with a further mol.; 0·7 mol. of formaldehyde was rapidly (2 min.) released. These results are consistent with the oxidation of the majority of 3-acetamido-3-deoxy-D-altrose in the furanose or acyclic form, rather than the pyranose form (V), both conformations of which (VII and VIII) are unstable because of axial interactions (see Reeves [10] and Barker and Shaw [11]).



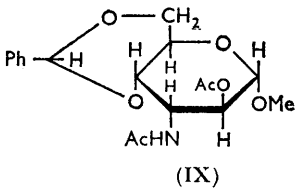
(VII)



(VIII)

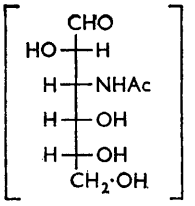
In 1943, Richtmyer and Hudson [12] suggested that the complex mutarotation of D-altrose could be explained if the crystalline material existed in the furanose form. It was of interest, therefore, to examine the oxidation of crystalline D-altrose by sodium metaperiodate solution buffered to pH 3·7; this gave 0·4 mol. of formaldehyde in 2·5 min. These results show that only 30% of 3-acetamido-3-deoxy-D-altrose and 60% of D-altrose are oxidized in the pyranose form, and that furanose and/or acyclic forms play a significant part.

McEvoy, Baker, and Weiss [13] found it possible to remove $C_{(1)}$ from 3-acetamido-3-deoxy-6-*O*-triphenylmethyl-D-altrose by oxidative cleavage with lead tetra-acetate, but with periodate the reaction was unsuccessful. They commented that the pyranose



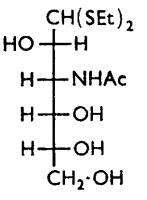
(IX)

H^+



(X)

EtSH
H^+



(XI)

configuration of the triphenylmethyl derivative had been assumed without evidence and hence this product was, or contained quantities of, the corresponding altrofuranose.

In direct contrast, 2-acetamido-2-deoxy-D-arabinose was prepared by the periodate cleavage of 3-acetamido-3-deoxy-D-mannopyranose,[14] presumably because the C1 chair conformation of 3-acetamido-3-deoxy-D-mannopyranose is more stable than that of the D-*altro*-isomer.

Attention was then turned to the disulphone method of shortening the carbon chain of

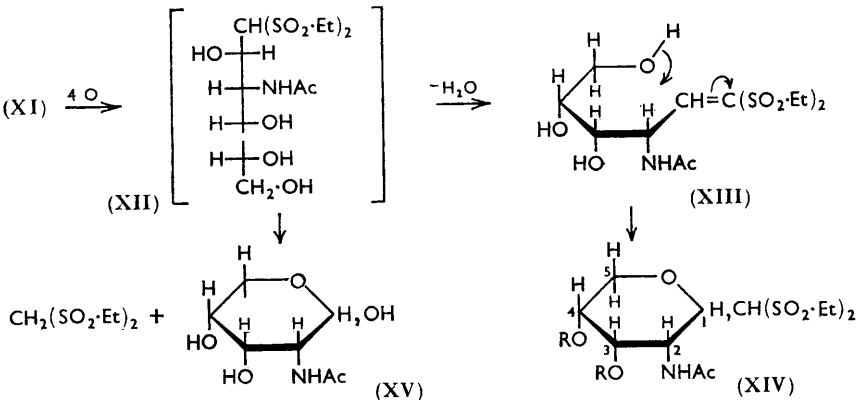
[8] Andrews, Hough, and Powell, *Chem. and Ind.*, 1956, 658.
[9] Hough, Taylor, Thomas, and Woods, *J.*, 1958, 1212.
[10] Reeves, *Adv. Carbohydrate Chem.*, 1951, **6**, 107.
[11] Barker and Shaw, *J.*, 1959, 584.
[12] Richtmyer and Hudson, *J. Amer. Chem. Soc.*, 1943, **65**, 740.
[13] McEvoy, Baker, and Weiss, *J. Amer. Chem. Soc.*, 1960, **82**, 209.
[14] Baer and Fischer, *J. Amer. Chem. Soc.*, 1960, **82**, 3709.

aldoses.[15,16] Treatment of 3-acetamido-3-deoxy-D-altrose at 0° with ethanethiol and concentrated hydrochloric acid [17] gave a complex mixture, as revealed by paper chromatography, from which 3-acetamido-3-deoxy-D-altrose diethyl dithioacetal (XI) crystallized.

A more convenient preparation with an improved yield (23%) of the dithioacetal (XI) from methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside was acetylation to give the methyl 3-acetamido-2-*O*-acetyl derivative [18] (IX) followed by treatment with concentrated hydrochloric acid and ethanethiol at room temperature. The latter reaction caused the removal of the benzylidene, glycosidic methoxyl, and 2-*O*-acetyl groups with simultaneous thioacetal formation from the resultant 3-acetamido-3-deoxy-D-altrose (X).

Oxidation of the dithioacetal (XI) with peroxypropionic acid in methanol at −10° was expected to give the diethylsulphonylpyranosylmethane derivative (XIV; R = H) by the formation of the hexenetriol (XIII) from the hexanetetraol (XII) followed by cyclization. (The dithioacetals of D-glucose, D-mannose, and D-galactose gave diethylsulphonylpyranosylmethanes by this process.[15]) However, paper chromatography of the product revealed another compound which, after separation, was shown to be 2-acetamido-2-deoxy-D-ribose (XV). This pentose was identical with that prepared similarly from 3-acetamido-3-deoxy-D-allose diethyl dithioacetal,[19] and undoubtedly arose by cleavage of the 1,2-bond in the unstable tetraol intermediate (XII).

The pyranose structure of the disulphone was supported by its behaviour in pyridine,



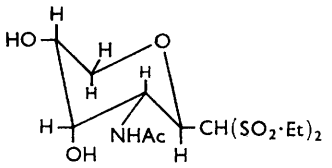
where no red colour developed, a reaction which is typical of the hex-1-ene derivatives (*e.g.*, XIII); and no cleavage to the acetamidopentose (XV) and diethylsulphonylmethane was observed, as would be expected [15] of the acyclic hexanetetraol (XII). The isolation of a crystalline triacetate (XIV; R = Ac) which was identical with that prepared in the same way [19] from 3-acetamido-3-deoxy-D-allose derivatives, confirmed the cyclic structure.

Conformational analysis was then used to predict the configuration at $C_{(1)}$, as in the case of other diethylsulphonylpyranosylmethanes.[15]

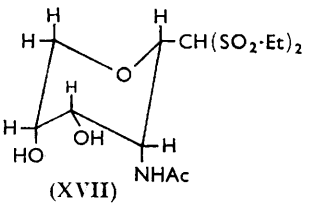
Two chair conformations of (2-acetamido-2-deoxy-D-ribopyranosyl)diethylsulphonylmethane (XIV; R = H) are possible in which the large, polar diethylsulphonylmethyl group is in an equatorial position. The 1C chair conformation (XVII) with the diethylsulphonylmethyl group in the α-configuration has a 2,4-diaxial interaction involving the large acetamido-group and a hydroxyl group. On the other hand, the C1 conformation (XVI) has only one axial substituent, namely, a 3-hydroxyl group, and hence this conformation, with the diethylsulphonylmethyl group in the β-configuration, is to be preferred.

[15] Hough and Taylor, *J.*, 1956, 970.
[16] Barker and MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 2297; MacDonald and Fischer, *J. Amer. Chem. Soc.*, 1952, **74**, 2087; *Biochim. Biophys. Acta*, 1953, **12**, 203.
[17] Hough and Taha, *J.*, 1956, 2042.
[18] Robertson and Myers, *Nature*, 1939, **143**, 640.
[19] Coxon and Hough, *Chem. and Ind.*, 1959, 1249.

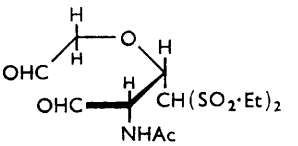
Since the glycosides of 2-acetamido-2-deoxy-D-ribose were not available, it was not possible to apply Hudson's isorotation rules directly [15] to the cyclic disulphone (XIV; R = H; $[M]_D$ −11,690°). The molecular rotations of methyl α-D-ribopyranoside [20] ($[M]_D$ +16,920°) and methyl β-D-ribopyranoside [21] ($[M]_D$ −17,260°) were therefore used as



(XVI)



(XVII)



(XVIII)

a basis for comparison. The value of B (−170°) gave a negative value for A (−11,520°), providing further support for the β-configuration of the diethylsulphonylmethyl group, and the cyclic disulphone is, therefore, termed (2-acetamido-2-deoxy-β-D-ribopyranosyl)-diethylsulphonylmethane (XVI).

As with other diethylsulphonylpyranosylmethanes,[15] (2-acetamido-2-deoxy-β-D-ribopyranosyl)diethylsulphonylmethane reacted with more periodate than is required for glycol cleavage because of breakdown of the dialdehyde (XVIII) due to the combined inductive effects of the sulphone and acetamido-groups. Thus, the disulphone consumed 2 mol. of periodate in 1 hr. and a further 2 mol. in the next 60 hr.

Experimental

Solutions were concentrated under reduced pressure. Optical rotations were measured for $CHCl_3$ solutions at 24° ± 1° unless otherwise stated. Paper chromatography was performed by the descending method at room temperature on Whatman No. 1 filter paper for qualitative purposes or on Whatman 3MM filter paper for preparative purposes, with the following mobile phases (i) butan-1-ol–pyridine–water (10 : 3 : 3 v/v), (ii) butan-1-ol–ethanol–water (40 : 11 : 19 v/v), (iii) benzene–ethanol–water (169 : 47 : 15 v/v; upper layer), (iv) ethyl acetate–acetic acid–water (9 : 2 : 2 v/v). Rates of movement of compounds are quoted relative to that of rhamnose (R_{Rh}) or the solvent front (R_F). The compounds were detected with the following sprays; (*a*) 1% w/v ninhydrin in butan-1-ol (for amino-derivatives), (*b*) 0·02M-sodium metaperiodate followed after 5 min. by 4% w/v ammoniacal silver nitrate reagent (for diols, triols, etc.), (*c*) 4% w/v ammoniacal silver nitrate (for reducing sugars and dithioacetals), (*d*) *p*-anisidine hydrochloride in butan-1-ol–ethanol–water (for reducing sugars), and (*e*) Elson–Morgan reagents [22] (for 2-acetamido-sugars). M. p.s were determined on a Kofler microheating stage. Infrared absorption spectra were determined in Nujol mulls with a Unicam S.P. 100 spectrometer. Decolorizations were carried out in alcoholic solutions by B.D.H. acid-washed charcoal, further washed before use with water followed by alcohol.

3-Amino-1,6-anhydro-3-deoxy-β-D-altropyranose (I) *Hydrochloride.*—Methyl 3-amino-4,6,-*O*-benzylidene-3-deoxy-α-D-altropyranoside [1,2] (5 g.) in 1% w/v hydrochloric acid (200 ml.) was heated at 100° for 22 hr. The cooled solution was washed with chloroform to remove benzaldehyde, decolorized, and concentrated to a syrup which crystallized when kept over sodium hydroxide. Recrystallization from methanol yielded the hydrochloride as cubes (1·2 g., 35%), m. p. 205—215° (decomp.), $[\alpha]_D^{21}$ −175° (*c* 0·51 in H_2O), R_{Rh} 0·36 (solvent i; brown spot with spray *a*) (Found: C, 36·6; H, 6·1; N, 7·0. Calc. for $C_6H_{12}ClNO_4$: C, 36·4; H, 6·1; N, 7·1%). Levene and Meyer [3] record m. p. 216° (decomp.), $[\alpha]_D^{20}$ −172° (*c* 1 in 2·5% HCl).

3-Acetamido-2,4-di-O-acetyl-1,6-anhydro-3-deoxy-β-D-altropyranose (II).—Methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside (64 g.) was hydrolysed in 4% w/v hydrochloric acid (720 ml.) at 100° for 48 hr. The cooled solution was then extracted with chloroform

[20] Barker and Smith, *J.*, 1954, 2151.
[21] Jackson and Hudson, *J. Amer. Chem. Soc.*, 1941, **63**, 1229.
[22] Kent and Whitehouse, "Biochemistry of the Amino-sugars," Butterworths, London, 1955, p. 164, and references therein.

(2 × 50 ml.) to remove benzaldehyde, concentrated to *ca.* one-third of the initial volume, and decolorized. Further concentration gave a pale green syrup of (mainly) 3-amino-1,6-anhydro-3-deoxy-β-D-altropyranose hydrochloride. The syrupy amino-derivative was treated with dry pyridine (270 ml.) and acetic anhydride (250 ml.) at 28° for 45 hr., and the solution was concentrated to remove pyridine and acid anhydride. The dark red solution was then poured on ice and sodium hydrogen carbonate, and the suspension was continuously extracted with chloroform for 3 hr. Evaporation of the extract afforded a brown syrup which was decolorized, and crystallized from ethanol, giving needles of the *triacetyl derivative* (41 g., 63% overall), m. p. 176—177° unchanged after a further recrystallization from ethanol. The derivative was soluble in water and had $[\alpha]_D$ −147° (*c* 0·44 in H_2O) (Found: C, 50·2; H, 6·3; N, 4·9; Ac, 41·3, 39·6. $C_{12}H_{17}NO_7$ requires C, 50·2; H, 6·0; N, 4·9; Ac, 45·0%), $\nu_{max.}$ 3300m and 1562s (NH), 1752s and 1738s (*O*-Ac), 1655s (*N*-Ac) cm.$^{-1}$.

3-*Acetamido*-1,6-*anhydro*-3-*deoxy*-β-D-*altropyranose* (III).—3-Acetamido-2,4-di-*O*-acetyl-1,6-anhydro-3-deoxy-β-D-altropyranose (1·01 g.) in methanol (25 ml.) was treated with liquid ammonia until the solution was saturated, and kept at room temperature for 3·5 hr. Concentration then gave a syrup, from which acetamide was removed by sublimation at 100°/15 mm. When seeded and triturated with methanol–acetone, the syrup crystallized, yielding the N-*acetyl derivative* (0·57 g., 80%), m. p. 159—160°, $[\alpha]_D$ −235° (*c* 1·14 in H_2O) (Found: C, 47·3; H, 6·6; N, 6·5; Ac, 22·5. $C_8H_{13}O_5N$ requires C, 47·3; H, 6·5; N, 6·9; Ac, 21·2%); this did not consume periodate during 48 hr.

3-*Acetamido*-1,2,4,6-*tetra*-O-*acetyl*-3-*deoxy*-αβ-*altropyranoses* (IV).—3-Acetamido-2,4-di-*O*-acetyl-1,6-anhydro-3-deoxy-β-D-altropyranose {1·06 g.; $[\alpha]_D$ −195° (*c* 4·24 in acetic anhydride)} was dissolved in acetic anhydride (50 ml.) containing concentrated sulphuric acid (1 ml.). After 0·5 hr. at room temperature the solution had $[\alpha]_D$ +44·2° (calc. as penta-acetyl derivative). unchanged after 18 hr. The colourless mixture was then poured into an ice-cold aqueous suspension of sodium hydrogen carbonate and extracted with chloroform (5 × 30 ml.). The extracts were washed with water, dried ($CaSO_4$), and concentrated to a syrupy mixture of penta-acetates (1·17 g., 81%), $[\alpha]_D$ +27·0° (*c* 4·66) (Found: Ac, 48. Calc. for $C_{16}H_{23}O_{10}N$: Ac, 55%). The use of 60% aqueous perchloric acid [7] (1·1 equiv.) in place of sulphuric acid gave a syrup of similar specific rotation. One preparation crystallized in part from methanol–ether to give a *penta-acetate* (0·16 g., 41%) that, recrystallized from methanol–ether, had m. p. 161°, $[\alpha]_D$ +4·0° (*c* 1·38%) (Found: C, 49·0; H, 6·2; N, 3·8. $C_{16}H_{23}NO_{10}$ requires C, 49·3; H, 6·0; N, 3·6%). The preparation of the crystalline derivative was not, however, reproducible, but on de-*O*-acetylation with ammonia the crystals yielded 3-acetamido-3-deoxy-D-altrose as did the syrup.

3-*Acetamido*-3-*deoxy*-D-*altrose* (V).—The syrupy penta-acetyl derivative (1·5 g.) in methanol (30 ml.) was added to aqueous ammonia (30 ml.; *d* 0·88) and the mixture kept at room temperature for 24 hr. Concentration of the solution then gave a pale yellow syrup of 3-*acetamido*-3-*deoxy*-D-*altrose*, R_{Rh} 0·80 [solvent i; sprays *b*, *c*, and *d* (yellow spot)]. The product was purified by chromatography on large sheets of Whatman 3MM paper, or by adsorption on a squat column of B.D.H. acid-washed charcoal [8] followed by elution with water. Crystallization of the reducing sugar was difficult, but occurred when a methanolic solution evaporated slowly at 0° during 2—3 months. The powder obtained, m. p. 143—146 (decomp.), recrystallized from methanol, then having m. p. 151—153° (decomp.), $[\alpha]_D$ −35° (constant; 24 hr.; *c* 1·28 in H_2O) (Found: C, 43·5; H, 7·1; N, 5·8. $C_8H_{15}NO_6$ requires C, 43·5; H, 6·9; N, 6·3%), $\nu_{max.}$ 3290s 3190s, (OH and NH), 1620s (*N*-Ac), 1568s (NH). De-*O*-acetylation with sodium methoxide in methanol followed by de-ionization with Amberlite IR-120 (H^+) resin, gave a lower yield owing to hydrolysis of the *N*-acetyl group. When 3-acetamido-3-deoxy-D-altrose was used for later preparations, it was more convenient to use the syrup obtained initially from the penta-acetyl derivative.

Methyl 3-*Acetamido*-2-O-*acetyl*-4,6-O-*benzylidene*-3-*deoxy*-α-D-*altropyranoside* (IX).—Methyl 3-amino-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside in pyridine–acetic anhydride yielded, by the usual procedure, the diacetyl derivative as plates, m. p. 199—200°, $[\alpha]_D^{22}$ +17° (*c* 1·47). Robertson and Myers [18] recorded m. p. 201°, $[\alpha]_D$ +14·6°.

3-*Acetamido*-3-*deoxy*-D-*altrose Diethyl Dithioacetal* (XI).—(*a*) 3-Acetamido-3-deoxy-D-altrose (0·35 g.) in ethanethiol (2 ml.) and concentrated hydrochloric acid (2·4 ml.; *d* 1·18) was shaken at 0° for 28 hr. The emulsion was then diluted with methanol (30 ml.) and neutralized with lead carbonate, and insoluble residues were filtered off and washed with hot methanol (30 ml.).

Concentration of the combined filtrate and washings gave a pale yellow syrup (0·37 g.) which was decolorized. Paper chromatography revealed a mixture of at least five components which had R_F 0·07, 0·17 (solvent i; sprays *a* and *b*), 0·45, 0·73, 0·82 (solvent i; spray *b*). The component with R_F 0·73 crystallized from methanol–ether, yielding *3-acetamido-3-deoxy-D-altrose diethyl dithioacetal* (0·127 g., 25%), m. p. 135—138°, that, recrystallized from methanol–ether and washed with methanol, had m. p. 146—147°, $[\alpha]_D$ +26·2° (*c* 1·05 in MeOH) (Found: C, 44·0; H, 7·7; N, 4·3; S, 19·3; Ac, 14·0. $C_{12}H_{25}NO_5S_2$ requires C, 44·0; H, 7·7; N, 4·3; S, 19·6; Ac, 13·2%).

(*b*) Methyl 3-acetamido-2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside (0·43 g.) was shaken with ethanethiol (2 ml.) and concentrated hydrochloric acid (2 ml.; *d* 1·18) at room temperature for 6·5 hr. The mixture was then diluted with methanol (30 ml.) and neutralized with lead carbonate, and the insoluble residues were filtered off and washed in hot methanol. Concentration of the combined filtrate and washings yielded an emulsion which was treated with acetic anhydride (3 ml.) overnight, in order to complete *N*-acetylation. The anhydride was then distilled off and a syrup obtained which was decolorized; crystallized from ethanol–ether it yielded 3-acetamido-3-deoxy-D-altrose diethyl dithioacetal (0·09 g., 23%), m. p. 144—145°, undepressed on admixture with the previous preparation. Paper chromatography of the mother-liquors revealed the same mixture as was obtained before, except for a faint spot near the solvent front (benzaldehyde diethyl dithioacetal ?).

When the above reaction was repeated at 0° for 22 hr., the 3-acetamido-3-deoxy-D-altrose dithioacetal was isolated in lower yield (8%). Acetylation of the dithioacetal in pyridine–acetic anhydride afforded the *tetra*-O-*acetate* which crystallized as rods, m. p. 110° (Found: C, 48·1; H, 6·6. $C_{20}H_{33}NO_9S_2$ requires C, 48·4; H, 6·7%).

Oxidation of 3-Acetamido-3-deoxy-D-altrose Diethyl Dithioacetal by Peroxypropionic Acid.—The diethyl dithioacetal (0·21 g.) in methanol (25 ml.) was cooled to −10°, and aqueous peroxypropionic acid [23] (5 ml.) added in small portions with shaking. The mixture was kept at −10° for 2·5 hr. and then concentrated to a colourless hygroscopic syrup from which traces of peroxypropionic acid were removed by repeated dissolution in methanol and reconcentration (yield 0·25 g.). Paper chromatography of the syrup, with spray *b*, showed the presence of two components with R_{Rh} 1·1 and 1·5 (solvent iv), and R_{Rh} 1·0 and 1·6 (solvent i). The two components of the syrup were separated by paper chromatography with solvent ii for 14 hr. The separated compounds were then detected with spray *b* and eluted from the appropriate zones with warm methanol. The slower moving component (R_{Rh} 1·1) was obtained as a syrup (0·048 g.) which crystallized from methanol–ether, to give *2-acetamido-2-deoxy-D-ribose* (XV) (0·018 g.), m. p. 136—139°, R_F 0·44 [solvent i; sprays *b*, *d* (orange spot), *c*, and *e* (violet spot)] (Found: C, 43·4; H, 6·8. $C_7H_{13}NO_5$ requires C, 44·0; H, 6·9%), $\nu_{max.}$ 3440s and 3350s (OH and NH), 1565s (NH), 1600s (*N*-Ac).

The faster-moving zone of the chromatogram (R_{Rh} 1·5) yielded (*2-acetamido-2-deoxy-β-D-ribopyranosyl*)*diethylsulphonylmethane* (XVI), a syrup (0·087 g.), $[\alpha]_D^{26}$ −31·3° (*c* 5·66 in MeOH) (Found: C, 38·8; H, 6·4; N, 3·8; S, 18·1; Ac, 13·9. $C_{12}H_{23}NO_8S_2$ requires C, 38·6; H, 6·2; N, 3·8; S, 17·2; Ac, 11·5%). The syrup did not give a red colour with dry pyridine, suggesting that unsaturated disulphones were absent.

(*2-Acetamido-3,4-di-O-acetyl-2-deoxy-β-D-ribopyranosyl*)*diethylsulphonylmethane* (XIV; R = Ac).—(2-Acetamido-2-deoxy-β-D-ribopyranosyl)diethylsulphonylmethane (0·08 g.) was dissolved in acetic anhydride (5 ml.), concentrated sulphuric acid (1 drop) added, and the mixture heated at 95—100° for 1 hr. The dark solution was then cooled to room temperature, poured into ice and sodium hydrogen carbonate, and extracted with chloroform (5 × 15 ml.). The combined extracts were washed with water, dried ($CaSO_4$), and concentrated to a pale yellow syrup which was decolorized (yield 0·094 g., 96%). Crystallization from acetone–light petroleum (b. p. 60—80°) afforded needles (0·035 g., 35%), m. p. 181—183°; recrystallized from the same solvents and washed with a little ethereal acetone, the *triacetyl derivative* had m. p. 183—185°, $[\alpha]_D$ −16·8° (*c* 1·34) (Found: C, 42·2; H, 6·0; N, 3·1; S, 13·1. $C_{16}H_{27}NO_{10}S_2$ requires C, 42·0; H, 6·0; N, 3·1; S, 14·0%), $\nu_{max.}$ 3300m and 1550s (NH), 1750s (*O*-Ac), 1650s (*N*-Ac).

Periodate Oxidations.—The compound (15—35 mg.) was made up to 100 ml. with water including sodium metaperiodate solution and buffer, if required. The uptake of periodate was

[23] d'Ans and Frey, *Ber.*, 1912, **45**, 1845.

determined by the neutral thiosulphate method.[24] Acid released was estimated by addition of ethylene glycol (2 ml.) to an aliquot part (5 or 10 ml.), followed by titration after 10 min. with 0·01N-sodium hydroxide to 1% w/v Methyl Red (screened with Methylene Blue).

Formaldehyde. The compound (2—5 mg.) was added to water (*ca.* 20 ml.) containing 0·2M-sodium metaperiodate (1·0 ml.), buffer (if required), and 0·1N-*p*-hydroxybenzaldehyde solution (1·0 ml.),[25] and made up to 25 ml. with water. Aliquot parts (1·0 ml.) were withdrawn and the formaldehyde liberated determined colorimetrically by the chromotropic acid method,[26] *meso*-erythritol being used as standard. Results are given in moles of either oxidant or product per mole of carbohydrate at various times (hr.).

(1) 3-Amino-1,6-anhydro-3-deoxy-β-D-altropyranose hydrochloride in unbuffered 0·024M-sodium metaperiodate.

Time	0·5	1	3	5·5	22
Uptake	1·77	1·83	1·93	2·0	2·0
Acid	0·6	0·8	0·9	1·0	0·9

(2) 3-Acetamido-3-deoxy-D-altrose in 0·01M-sodium metaperiodate at pH 3·7 (acetate buffer).

Time	0·03	0·25	0·5	1·0	2·0	4	5	7	12	24
Uptake	—	1·27	1·61	1·96	2·15	2·32	—	2·58	2·78	2·94
CH_2O	0·67	0·67	0·68	—	—	—	0·73	—	—	—

(3) D-Altrose in 0·012M-periodate at pH 3·7 (acetate buffer).

Time	0·04	0·08	0·5	2·5	4
CH_2O	0·37	0·40	0·44	0·44	0·44

(4) (2-Acetamido-2-deoxy-β-D-ribopyranosyl)diethylsulphonylmethane in unbuffered 0·015M-periodate.

Time	0·25	0·75	1·5	3·0	7	24	46	73
Uptake	1·39	1·93	2·28	2·74	3·24	3·68	3·88	4·11
Acid	0·27	0·32	0·61	0·91	1·43	1·96	2·18	2·30

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[24] Neumüller and Vasseur, *Arkiv Kemi*, 1953, **5**, 235.
[25] O'Dea, *Chem. and Ind.*, 1953, 1338.
[26] O'Dea and Gibbons, *Biochem. J.*, 1953, 580.