320. 3-*Acetamido*-3-*deoxy*-D-*allose Diethyl Dithioacetal and its Oxidation by Peroxypropionic Acid.*[1]

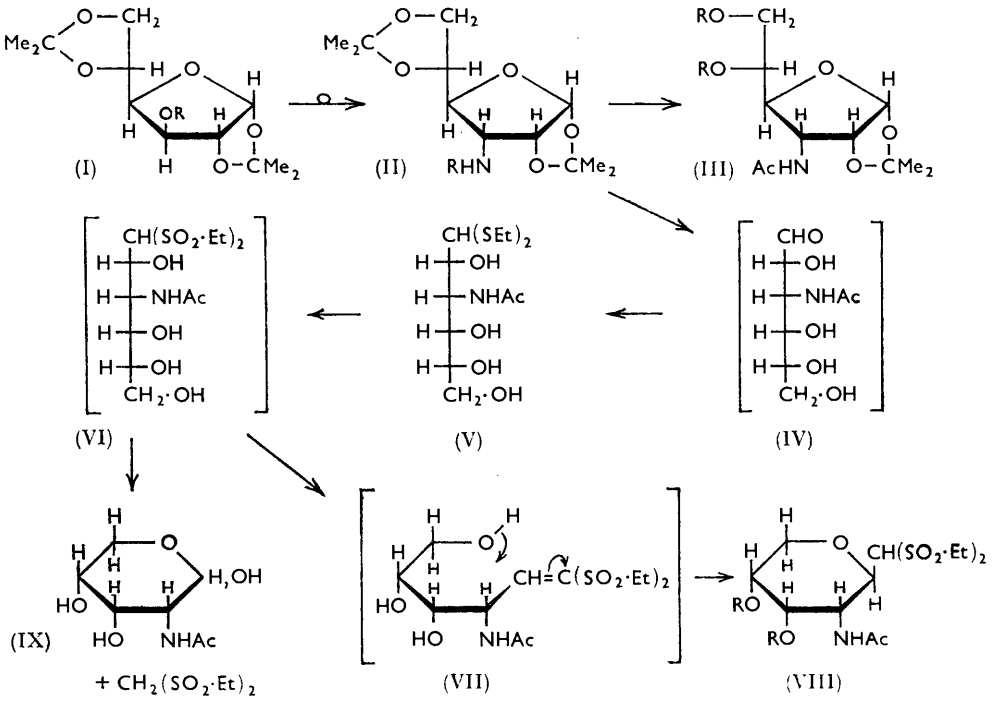
By Bruce Coxon and L. Hough.

The reactions of 1,2:5,6-di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose with ammonia and with hydrazine proceed with inversion at $C_{(3)}$ to give D-allofuranose derivatives. The products were converted into 3-acetamido-3-deoxy-D-allose diethyl dithioacetal which was oxidised with peroxypropionic acid to a mixture of (2-acetamido-2-deoxy-β-D-ribopyranosyl)-diethylsulphonyl methane, 2-acetamido-2-deoxy-D-ribose, and diethylsulphonylmethane. The mechanism of this reaction is discussed.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose (I; R = tosyl) reacts with ammonia,[2] dimethylamine,[3] and hydrazine [4] by nucleophilic substitution of the toluene-*p*-sulphonyloxy-group to give the 3-amino-, 3-dimethylamino-, and 3-hydrazino-derivatives,

[1] For a preliminary account of some of this work, see Coxon and Hough, *Chem. and Ind.*, 1959, 1249.
[2] Freundenberg, Burkhart, and Braun, *Ber.*, 1926, **59**, 714.
[3] Freundenberg and Smeykal, *Ber.*, 1926, **59**, 100.
[4] Freundenberg and Brauns, *Ber.*, 1922, **55**, 3233.

in which Freundenberg *et al.* considered that the D-*gluco*-configuration was retained. This view persisted [5,6] until 1956, when Cope and Shen [7] questioned the assumed stereochemical course of the reaction on the basis of a study of the differences in reactivity of 1,4:3,6-dianhydrohexitol ditoluene-*p*-sulphonates with a variety of nucleophilic reagents. They found good evidence for the assignment of the S_N2 mechanism to these reactions, and



hence the reaction of the 3-*O*-tosylglucofuranose derivative (I; R = tosyl) with nucleophilic reagents was more likely to lead to stereochemical inversion at $C_{(3)}$, to give, *e.g.*, derivatives of type (II). In order to determine the stereochemical course of this reaction we have compared the diethylsulphonyl derivative prepared from the above 3-amino-3-deoxy-D-hexose with a similar derivative [8] of 3-acetamido-3-deoxy-D-altrose. The diethyl dithioacetal of the latter was oxidized with peroxypropionic acid to give, by cyclization of the intermediary D-*ribo*-3-acetamido-1,1-diethylsulphonyl-4,5,6-trihydroxyhex-1-ene (VII), (2-acetamido-2-deoxy-β-D-ribopyranosyl)diethylsulphonylmethane (VIII; R = H),* which should also be obtained from the configurationally related 3-acetamido-3-deoxy-D-allose.

As in the previous work,[2] the reaction of 1,2:5,6-di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose (I; R = tosyl) with methanolic ammonia under pressure at 170° gave a rather impure 3-aminohexofuranose derivative in low yield (11—16%). In an effort to improve the yield of this replacement product, the reaction of 1,2:5,6-di-*O*-isopropylidene-3-*O*-(nitrobenzene-*p*-sulphonyl)-α-D-glucofuranose (I; R = nitrobenzene-*p*-sulphonyl) with

* According to a previous system of nomenclature,[9] this cyclic disulphone (VIII; R = H) would be termed D-*allo*-3-acetamido-2,6-epoxy-1,1-diethylsulphonyl 4,5-dihydroxyhexane.

[5] Peat and Wiggins, *J.*, 1938, 1810.
[6] Wolfrom, Shafizadeh, and Armstrong *J. Amer. Chem. Soc.*, 1958, **80**, 4885.
[7] Cope and Shen, *J. Amer. Chem. Soc.*, 1956, **78**, 3177.
[8] Coxon and Hough, *J.*, 1961, 1463.
[9] Hough and Taylor, *J.*, 1956, 970.

ammonia under pressure was attempted (cf. Tipson [10]), since it was expected that the *p*-nitro-substituent would facilitate electron-recession in the departing group. The only crystalline product obtained was 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, presumably formed by fission of the sulphur–oxygen bond of the sulphonyl ester, by nucleophilic attack by ammonia, at sulphur instead of at carbon,[11] resulting in retention of configuration.

Improved yields [6,12] have been obtained by treatment of 1,2:5,6-di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose with hydrazine at 140°, and subsequent catalytic hydrogenation of the 3-deoxy-3-hydrazino-derivative.

A more convenient reaction was obtained by boiling the 3-*O*-tosyl derivative with hydrazine under reflux in an atmosphere of nitrogen, conditions somewhat less drastic than those used previously.[4,6] The 3-deoxy-3-hydrazino-derivative was unstable in air, and so it was hydrogenated immediately to give the 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene derivative (57% yield) which was identical with that prepared by direct ammonolysis. The 3-amino-3-deoxy-derivative with acetic anhydride–pyridine gave the 3-acetamido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-hexose.†

Treatment of this 3-acetamido-3-deoxy-1,2:5,6-di-*O*-isopropylidenehexose with ethanethiol and hydrochloric acid at 0° for 24 hr. afforded the 3-acetamido-3-deoxyhexose diethyl dithioacetal. Oxidation of the latter by peroxypropionic acid in methanol at either −20° or −10° gave a mixture of (2-acetamido-2-deoxy-β-D-ribopyranosyl)diethylsulphonylmethane (VIII; R = H), 2-acetamido-2-deoxy-D-ribose (IX), and diethylsulphonylmethane, which was separated by either paper chromatography or solvent extraction. The cyclic disulphone (VIII; R = H), its di-*O*-acetate (VIII; R = Ac), and 2-acetamido-2-deoxy-D-ribose were identical with those prepared previously [8] from 3-acetamido-3-deoxy-D-altrose diethyl dithioacetal.

Thus application of a series of reactions to the diethyl dithioacetals of 3-acetamido-3-deoxy-D-altrose [8] and 3-acetamido-3-deoxy-D-allose, involving modifications of the asymmetry only at position 2, established without doubt that the ammonolysis and hydrazinolysis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose (I; R = tosyl) proceeded with stereochemical inversion at position 3 to give derivatives of α-D-allofuranose (II).

An alternative proof of this inversion was described by Lemieux and Chu [12] who converted the 3-deoxy-3-hydrazino-derivative (II; R = NH_2) through the 3-amino-3-deoxy-derivative (II; R = H) into 3-amino-3-deoxy-D-ribose.

In order to establish firmly that the di-*O*-acetate (VIII; R = Ac) was not a derivative of the hex-1-ene (VII), the acetate (XII) of the latter was prepared by a method used by MacDonald and Fischer [13] to prepare D-*arabo*-3,4,5,6-tetra-*O*-acetyl-1,1-diethylsulphonylhex-1-ene.

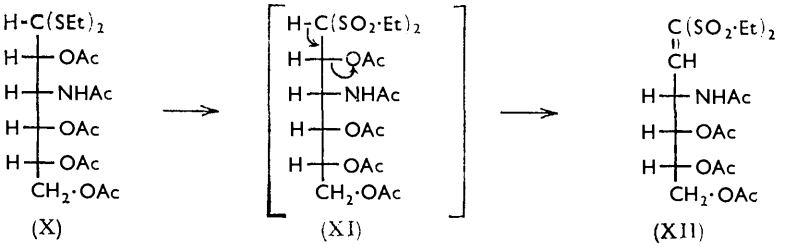
Acetylation of 3-acetamido-3-deoxy-D-allose diethyl dithioacetal (V) in pyridine–acetic anhydride afforded 3-acetamido-2,4,5,6-tetra-*O*-acetyl-3-deoxy-D-allose diethyl dithioacetal (X) which, on oxidation with peroxypropionic acid, yielded D-*ribo*-3-acetamido-4,5,6-tri-*O*-acetyl-1,1-diethylsulphonylhex-1-ene (XII) through the intermediary saturated 1,1-diethylsulphonyl derivative (XI) which had lost the elements of acetic acid. This hex-1-ene derivative (XII) differed from the di-*O*-acetate of the cyclic disulphone (VIII; R = Ac).

The formation of 2-acetamido-2-deoxy-D-ribose in the oxidations of 3-acetamido-3-deoxy-D-altrose [8] and 3-acetamido-3-deoxy-D-allose diethyl dithioacetal was a novel feature of these reactions, since it occurred under non-alkaline conditions. This pentose derivative probably arose from the acyclic saturated disulphones (*e.g.*, VI) since these are

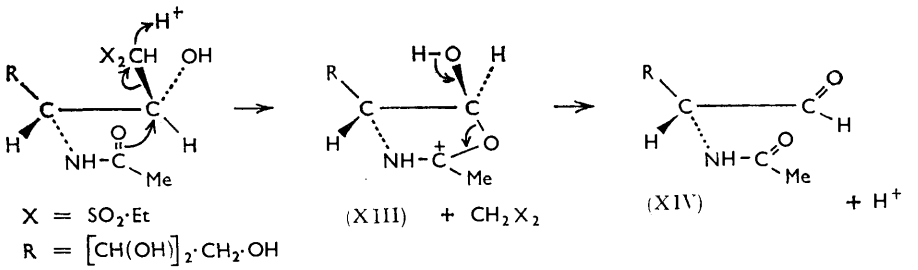
† When a solution of this product in chloroform was washed with dilute acid, 3-acetamido-3-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose (III; R = H) was obtained as a by-product, and was characterized as 3-acetamido-5,6-di-*O*-acetyl-3-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose (III; R = Ac).

[10] Tipson, *Adv. Carbohydrate Chem.*, 1953, **8**, 211.
[11] Hine, " Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1956, p. 281.
[12] Lemieux and Chu, *J. Amer. Chem. Soc.*, 1958, **80**, 4745.
[13] MacDonald and Fischer, *J. Amer. Chem. Soc.*, 1952, **74**, 2087.

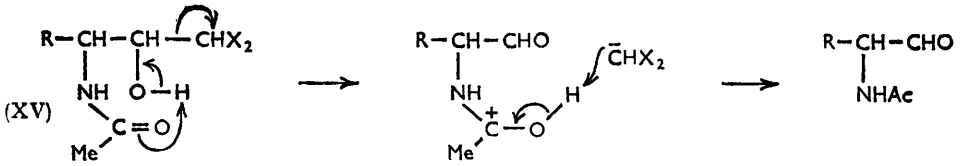
the most sensitive of the disulphones to cleavage with concomitant formation of diethylsulphonylmethane.[9] Since oxidations of D-altrose diethyl dithioacetal under the same conditions[14] did not produce any cleavage to pentose, it appears that the acetamido-group facilitated the production of 2-acetamido-2-deoxy-D-ribose by a reaction which was competitive with the formation of the 1,1-diethylsulphonylhex-1-enc (VII).



Neighbouring-group participation is possible in which the amide-oxygen attacks $C_{(2)}$ (which will be cationoid because of adjacent electrophilic substituents) with simultaneous ejection of the diethylsulphonylmethyl anion to give a cyclic carbonium ion (XIII) which would then collapse to give 2-acetamido-2-deoxy-D-ribose (XIV).



Alternatively, the weakly basic properties of the amide group could assist in the removal of the hydrogen of the hydroxyl at $C_{(2)}$ of the saturated disulphone (XV).



Pauling[15] has assessed the basic constant of amides as approximately 1×10^{-20} and this very weak basicity is almost certainly due to protonation of the carbonyl-oxygen atom, since addition of a proton to the nitrogen atom would inhibit the resonance of the amide group.[16]

Experimental

Details relevant to chromatography, presentation of infrared data, etc., are given in the preceding paper.[8]

1,2:5,6-*Di*-O-*isopropylidene*-3-O-*nitrobenzene*-p-*sulphonyl*-α-D-*glucofuranose* (I; R = nitrobenzene-*p*-sulphonyl).—1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (21·3 g.) in dry pyridine

[14] Coxon and Hough, unpublished results.
[15] Pauling, " The Nature of the Chemical Bond," Oxford University Press, London, 1940, 208.
[16] Wheland, " Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, 1955, 361.

(20 ml.) was cooled to 0° and a solution of nitrobenzene-*p*-sulphonyl chloride (20 g.; 1·1 mol.) in dry pyridine (25 ml.) was added dropwise with cooling and stirring. At this stage, the mixture was diluted with chloroform (10 ml.) to decrease its viscosity and kept at room temperature with stirring for 26 hr. Water was then added in small quantities with cooling and stirring, and the solution was poured into water and extracted with chloroform (4 × 100 ml.). The combined extracts were washed successively with cooled 2N-hydrochloric acid (2 × 200 ml.), saturated sodium hydrogen carbonate solution, and water, and dried (Na_2SO_4). Concentration gave a brown syrup which, after decolorization, crystallized as square prisms (29·8 g., 82%), m. p. 106—109°. Recrystallized twice from aqueous ethanol, the *sulphonate* had m. p. 110°, $[\alpha]_D$ −81·2° (*c* 3·99) (Found: C, 48·8; H, 5·1; N, 2·9. $C_{18}H_{23}NO_{10}S$ requires C, 48·5; H, 5·2; N, 3·1%).

Attempted Ammonolysis of the Nitrobenzene-p-*sulphonate.*—The sulphonate (12 g.) was suspended in methanol (500 ml.) saturated with anhydrous ammonia at *ca.* −30° (acetone–carbon dioxide). The mixture was sealed in a steel autoclave and heated at 165°/40 atm. for 45 hr. The dark brown solution was then concentrated to a black tar, to which 15% w/v potassium hydroxide (90 ml.) was added, and the mixture was extracted with ether (4 × 100 ml.). Concentration of the combined ethereal extracts gave a brown syrup which was decolorized and crystallized, giving needles of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (1·2 g., 17%), m. p. 107—109°, depressed to 94° on admixture with starting material. Washed with ether, the crystals had m. p. 110—111°, undepressed on admixture with authentic di-*O*-isopropylidene-α-D-glucofuranose.

3-*Deoxy*-3-*hydrazino*-1,2:5,6-*di*-O-*isopropylidene*-α-D-*allofuranose* (II; R = NH_2).—1,2:5,6-Di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose (20 g.) was heated under reflux for 25 hr. with 98% hydrazine (50 ml.) in a stream of oxygen-free nitrogen. The clear solution was then allowed to cool and extracted with ether (3 × 50 ml.), and the combined extracts were washed with 50% w/v potassium hydroxide (10 ml.) and dried (K_2CO_3). Concentration followed by drying at room temperature/1 mm. gave white crystals (11·0 g., 83%) which, after being washed with a little cold ether, had m. p. 97—100°, R_F 0·96 (solvent iii; sprays *a* and *c*). The hydrazino-derivative reduced Tollens's reagent in the cold and Benedict's reagent when heated, but was unstable in air; consequently each product was immediately reduced to the 3-amino-derivative.

3-*Amino*-3-*deoxy*-1,2:5,6-*di*-O-*isopropylidene*-α-D-*allofuranose* (II; R = H).—The hydrazino-derivative (11 g.) in ethanol (200 ml.) was hydrogenated in the presence of Raney nickel catalyst (15 g.), at 65 lb. per sq. in. for 18 hr. at *ca.* 80° in the Edwards apparatus. The catalyst was then filtered off through Celite filter aid, and the ethanolic solution concentrated to a crystalline residue, which, recrystallized from ethanol–light petroleum (b. p. 40—60°), yielded the 3-amino-derivative as needles (7·15 g., 69%). A further recrystallization from the same solvent pair gave the pure product which had m. p. 92—93°, $[\alpha]_D$ +32·7° (*c* 2·39), R_F 0·84 (solvent iii; spray *a*) (Found: C, 55·4; H, 8·0; N, 5·1. Calc. for $C_{12}H_{21}NO_5$: C, 55·6; H, 8·2; N, 5·4%). This amino-derivative was also prepared in 11% yield by the reaction [2] of methanolic ammonia with 1,2:5,6-di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuranose at 170° and had m. p. and mixed m. p. 91—93°, $[\alpha]_D$ +36° (*c* 1·25).

3-*Acetamido*-3-*deoxy*-1,2:5,6-*di*-O-*isopropylidene*-α-D-*allofuranose* (II; R = Ac).—To a solution of 3-amino-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (2·53 g.) in dry pyridine (15 ml.) was added acetic anhydride (15 ml.), and the mixture kept at room temperature for 13 hr., then poured into ice-water and extracted into chloroform (4 × 30 ml.). The combined extracts were washed successively with cold 2N-hydrochloric acid (3 × 30 ml.), saturated sodium hydrogen carbonate (30 ml.), and water, and then dried (Na_2SO_4). The pale yellow syrup obtained on concentration crystallized immediately, and was decolorized. Recrystallization from light petroleum (b. p. 80—100°) containing a little ethanol gave the *N*-acetyl derivative as rods (2·15 g., 73%), m. p. 130°, $[\alpha]_D$ +71·8° (*c* 2·12) (Found: C, 55·5; H, 7·5; N, 4·4. Calc. for $C_{14}H_{23}NO_6$: C, 55·8; H, 7·7; N, 4·6%), $\nu_{max.}$ 3370m and 1538s (NH), 1680s cm.$^{-1}$ (N-Ac). Lemieux and Chu [12] record m. p. 127—128°, and $[\alpha]_D$ +71·3°. In one particular preparation, the acetamido-derivative was impure and acetylation of this product as above, followed by crystallization from water, yielded 3-*acetamido*-5,6-*di*-O-*acetyl*-3-*deoxy*-1,2-O-*isopropylidene*-α-D-*allofuranose* (III; R = Ac) as needles, m. p. 162—164°. Recrystallized from water, the triacetate had m. p. 164—165°, depressed to 120—140° on admixture with the di-*O*-isopropylidene derivative, and had $[\alpha]_D$ +63·9° (*c* 2·00) (Found: C, 51·9; H, 6·7; N, 4·3. $C_{15}H_{23}NO_8$ requires C, 52·2; H, 6·7; N, 4·1%), $\nu_{max.}$, 3400m and 1530s (NH), 1753s and 1730s (*O*-Ac), 1680s cm.$^{-1}$

N-Ac). Later experience suggested that a better procedure for isolating the *N*-acetate of the di-*O*-isopropylidene-amino-derivative was to omit the acid-washing of the chloroform extract.

3-Acetamido-3-deoxy-1,2-O-isopropylidene-α-D-allofuranose (III; R = H).—The triacetate (1·22 g.) was dissolved in methanol (40 ml.) and aqueous ammonia (40 ml.; *d* 0·88) was added. The mixture was kept at room temperature for 38 hr.; ammonia was then removed under reduced pressure, and acetate ions by passage of the solution through Amberlite IR-4B(OH) resin. Concentration gave a brown syrup which crystallized after decolorization as needles (0·68 g., 74%). Recrystallized twice from methanol–ether, the *N*-acetyl derivative had m. p. 158—159°, $[\alpha]_D$ +150° (*c* 1·89 in H_2O), R_{Rh} 1·7 (solvent i; spray *b*) (Found: C, 50·4; H, 7·3; N, 5·4; Ac, 18·5. Calc. for $C_{11}H_{19}NO_6$: C, 50·5; H, 7·3; N, 5·4; Ac, 16·5%). Lemieux and Chu [12] record m. p. 157—158°.

Periodate oxidation gave the following results:

Time (hr.)	0·5	18·5	43
IO_4 consumed (mole)	0·92	1·01	1·01

3-Acetamido-3-deoxy-D-allose Diethyl Dithioacetal (V).—3-Acetamido-3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (1·5 g.) was treated with ethanethiol (8 ml.) and cooled to 0°. Concentrated hydrochloric acid (10 ml.; *d* 1·18) was added and the mixture shaken at 0°. After 24 hr., the mixture was diluted with methanol (100 ml.) and neutralized (lead carbonate), and the insoluble residues were filtered off and washed with hot methanol (150 ml.). Concentration of the combined filtrate and washings gave a white solid which was recrystallized from ethanol–light petroleum (b. p. 80—100°) and washed with a little light petroleum, yielding the *dithioacetal* as plates (0·9 g., 55%); recrystallized from ethanol–light petroleum (b. p. 80—100°), this had m. p. 160°, $[\alpha]_D$ −24·5° (*c* 1·88 in MeOH), R_{Rh} 1·9 (solvent i; sprays *b* and *c*) (Found: C, 44·1; H, 7·9; N, 4·0; S, 19·6; Ac, 15·4, 15·4. $C_{12}H_{25}NO_5S_2$ requires C, 44·0; H, 7·7; N, 4·3; S, 19·6; Ac, 13·2%).

Oxidation of 3-Acetamido-3-deoxy-D-allose Diethyl Dithioacetal by Peroxypropionic Acid.—The dithioacetal (0·74 g.) in methanol (20 ml.) was cooled to −20° (ice–salt), aqueous peroxypropionic acid (12 ml.) added dropwise with shaking, and the mixture kept at −20° for 1 hr. Concentration gave a hygroscopic syrup from which traces of peroxypropionic acid were removed by repeated dissolution in methanol and reconcentration (yield 0·94 g.). Paper chromatography of the syrup with spray *b* showed the presence of two components, R_{Rh} 1·1 and 1·5 (solvent iv) and R_F 0·44 and 0·63 (solvent i). Two methods of working up were used.

(a) *By paper chromatography.* The syrup (0·75 g.) was separated by chromatography on three large sheets of Whatman 3MM filter paper, solvent i being used for 22 hr. and the acetamido-derivatives were extracted from the appropriate parts of the chromatograms with hot methanol. The slower-moving component (R_F 0·44) was obtained as a syrup (0·119 g.) which slowly crystallized, yielding fine needles (0·064 g.) of 2-acetamido-2-deoxy-D-ribose. Recrystallized thrice from methanol–ether, the pentose derivative had m. p. 138—141°, $[\alpha]_D^{26}$ −69° (2 min.) ⟶ −36° (15 min. final, *c* 0·90 in H_2O), R_F 0·44 [solvent i; sprays *b*, *d* (orange spot), and *e* (violet spot)] (Found: C, 44·2; H, 7·0; N, 7·3; Ac, 20·6. Calc. for $C_7H_{13}NO_5$: C, 44·0; H, 6·9; N, 7·3; Ac, 22·5%), $\nu_{max.}$ 3440s and 3350s (OH and NH), 1565s (NH), 1600s cm.$^{-1}$ (*N*-Ac). It had identical infrared spectrum and mixed m. p. 136—139° with the product (m. p. 136—139°) obtained by oxidation of 3-acetamido-3-deoxy-D-altrose diethyl dithioacetal.[8] Kuhn and Baschang [17] record m. p. 141—143°, $[\alpha]_D$ −73·2° (2 min.) ⟶ −39° (1 hr.).

The faster-moving component (R_F 0·63) was a syrup (0·344 g.) which partially crystallized on trituration with methanol, giving needles, m. p. 101—102° undepressed on admixture with authentic diethylsulphonylmethane. The mother-liquors were diluted with water (50 ml.) and extracted with benzene (3 × 20 ml.). Concentration of the benzene extracts gave more diethylsulphonylmethane and evaporation of the aqueous layer gave a hygroscopic syrup of (2-acetamido-2-deoxy-β-D-ribopyranosyl)diethylsulphonylmethane (0·27 g.), $[\alpha]_D$ −29·6° (*c* 4·60 in MeOH) (Found: C, 38·5; H, 6·1; N, 3·8; S, 17·9; Ac, 12·2%; equiv., 389. Calc. for $C_{12}H_{23}NO_8S_2$: C, 38·6; H, 6·2; N, 3·8; S, 17·2; Ac, 11·5%; *M*, 374), $\nu_{max.}$ 3520—3400s (OH and NH), 1667s (*N*-Ac), 1532 cm.$^{-1}$ (NH). The disulphone gave only a pale yellow colour with dry pyridine even after prolonged standing.

(b) *By solvent extraction.* The mixture of disulphone, pentose, and diethylsulphonylmethane was separated on a larger scale by the following procedure. (i) Cold chloroform-extraction of a

[17] Kuhn and Baschang, *Annalen*, 1959, **628**, 193.

20% aqueous solution of the syrupy mixture removed diethylsulphonylmethane and a small quantity of disulphone. (ii) Continuous chloroform-extraction of the aqueous layer for 2 days yielded pure disulphone on concentration of the extract. (iii) Evaporation of the remaining aqueous layer gave 2-acetamido-2-deoxy-D-ribose.

(2-*Acetamido*-3,4-*di*-O-*acetyl*-2-*deoxy*-β-D-*ribopyranosyl*)*diethylsulphonylmethane* (VIII; R = Ac).—A solution of (2-acetamido-2-deoxy-β-D-ribopyranosyl)diethylsulphonylmethane (0·18 g.) in acetic anhydride (6 ml.) was heated with concentrated sulphuric acid (2 drops) at 95—100° for 0·5 hr. After cooling to room temperature, the mixture was poured into ice and sodium hydrogen carbonate and extracted with chloroform (5 × 30 ml.). The combined extracts were washed with water and dried ($CaSO_4$). Concentration gave a pale yellow syrup which was decolorized, yielding a syrup (0·2 g., 91%) which crystallized from acetone–light petroleum (b. p. 80—100°). Recrystallized from the same solvent pair and washed with ethereal acetone, the triacetate had m. p. 183—185°, $[\alpha]_D$ −17·5° (*c* 1·09) (Found: C, 41·8; H, 5·9; N, 3·0; S, 12·3; Ac, 27·6. Calc. for $C_{16}H_{27}NO_{10}S_2$: C, 42·0; H, 6·0; N, 3·1; S, 14·0; Ac, 28·2%), $\nu_{max.}$ 3300m and 1550s (NH), 1750s (*O*-Ac), 1650s cm.$^{-1}$ (*N*-Ac). The product had mixed m. p. 183—185° and was identical in infrared spectrum and *X*-ray powder photograph with the authentic specimen {m. p. 183—185°, $[\alpha]_D$ −16·8° (*c* 1·34)} obtained from 3-acetamido-3-deoxy-D-altrose.[8]

Acetylation of the syrupy disulphone (VIII; R = H) in acetic anhydride–pyridine for 3 days gave the same crystalline triacetate as described above.

3-*Acetamido*-2,4,5,6-*tetra*-O-*acetyl*-3-*deoxy*-D-*allose Diethyl Dithioacetal* (X).—3-Acetamido-3-deoxy-D-allose diethyl dithioacetal (1·0 g.) was suspended in dry pyridine (20 ml.) and acetic anhydride (20 ml.) added. After 19 hr. at room temperature, the mixture was poured into ice-water containing sodium hydrogen carbonate and extracted into chloroform (5 × 20 ml.). The combined extracts were washed successively with cold 2N-hydrochloric acid (2 × 50 ml.), saturated sodium hydrogen carbonate solution, and water. Concentration gave a pale yellow syrup which was decolorized. Dilution of the methanolic solution with water yielded clusters of highly reflecting needles, m. p. 124—125° (1·02 g., 67%). Recrystallized from aqueous methanol, the *penta-acetate* had m. p. 125°, $[\alpha]_D$ +30·0° (*c* 2·33) (Found: C, 48·1; H, 6·9; N, 2·8; S, 12·4; Ac, 36·8. $C_{20}H_{33}NO_9S_2$ requires C, 48·4; H, 6·7; N, 2·8; S, 12·9; Ac, 43·4%).

D-ribo-3-*Acetamido*-4,5,6-*tri*-O-*acetyl*-1,1-*diethylsulphonylhex*-1-*ene* (XII).—3-Acetamido-2,4,5,6-tetra-*O*-acetyl-3-deoxy-D-allose diethyl dithioacetal (0·56 g.) in methanol (20 ml.) was cooled to −8°, and aqueous peroxypropionic acid (6 ml.) was added. The mixture was kept at −5° for 1 hr., then concentrated to a syrup (0·61 g.) which crystallized from methanol–ether as needles, m. p. 135—137° (0·35 g., 61%). Recrystallized from methanol–ether, the *hexene* had m. p. 137°, $[\alpha]_D$ +49° (*c* 1·44) (Found: C, 43·1; H, 6·0; N, 2·8; S, 12·1; Ac, 32·9. $C_{18}H_{29}NO_{11}S_2$ requires C, 43·2; H, 5·9; N, 2·8; S, 12·9; Ac, 34·5%), $\nu_{max.}$ 3370m and 1520m (NH), 1750s (*O*-Ac), 1670s (*N*-Ac), 1620w cm.$^{-1}$ (C=C). The compound absorbed below 220 mμ.

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