203. *Diethylsulphonyl Derivatives of* D-glycero-L-manno-*Heptose and* D-glycero-L-gluco-*Heptose.*

By L. D. Hall, L. Hough, S. H. Shute, and T. J. Taylor.

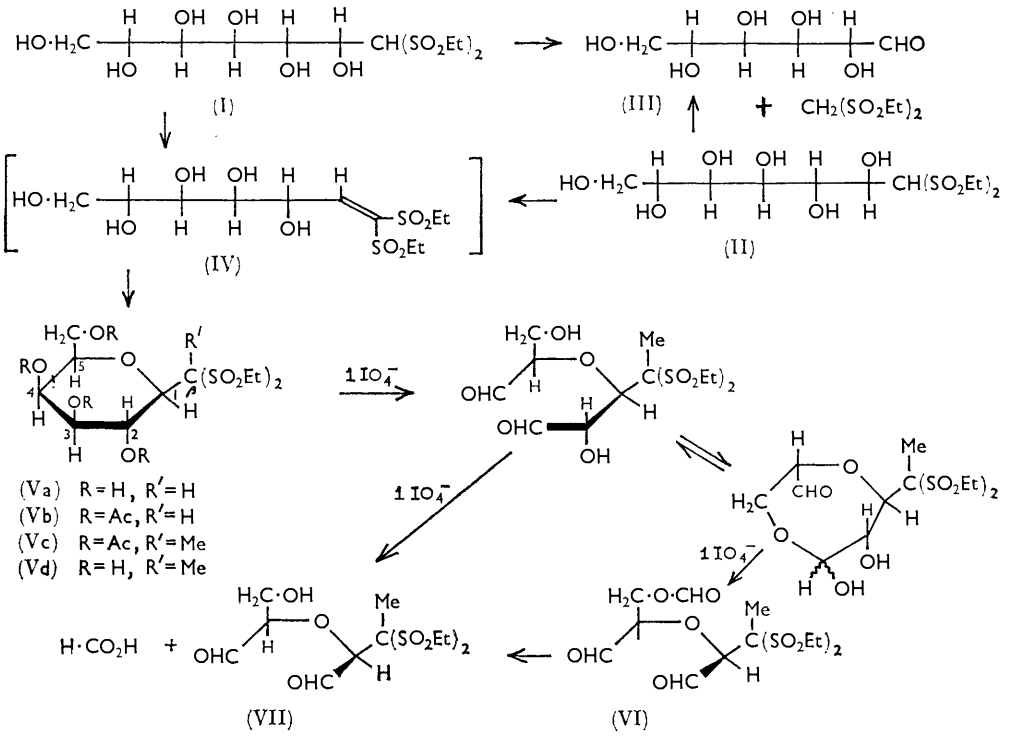
Acyclic 1,1-diethylsulphonyl derivatives of D-*glycero*-L-*manno*-heptose and D-*glycero*-L-*gluco*-heptose have been prepared by oxidation of their diethyl dithioacetals. Heating of these sulphones in water caused cyclodehydration, giving, as the main product, diethylsulphonyl-β-D-galactopyranosylmethane. First-order analysis of the proton magnetic resonance spectra of the tetra-acetate of the cyclic sulphone and its *C*-methyl derivative confirmed the structures assigned from periodate oxidation and molecular rotation studies.

1,1-Diethylsulphonyl derivatives of aldohexoses undergo cyclodehydration to pyranosylmethanes [1] by intramolecular attack of the terminal primary hydroxyl group on the double bond of an intermediary hex-1-ene, and it was of interest to examine the behaviour of an aldoheptose sulphone under similar conditions of cyclisation; the heptose sulphone was also required for mechanistic studies. 1-Deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol and its D-*glycero*-L-gluco-epimer [2] were transformed into the corresponding aldoheptoses by the Nef reaction.[3] The derived dithioacetals were then oxidised to the crystalline acyclic sulphones (I) and (II), respectively. In each case the reaction mixture was shown by paper chromatography to contain a material of higher R_F, later identified as the β-pyranosylmethane (Va). This compound was also produced, together with traces of other components including D-galactose (III), on attempted recrystallisation of the acyclic sulphones (I) and (II) from water. This behaviour resembles that of 1,1-diethylsulphonyl-D-*manno*-2,3,4,5,6-pentahydroxyhexane and similar compounds.[1,4,5] The acyclic sulphones (I) and (II) showed considerable differences in water solubility and subsequent ease of cyclisation, the D-*glycero*-L-*gluco*-epimer (II) being very soluble and easily cyclised compared with the poorly soluble D-*glycero*-L-*manno*-epimer (I). The cyclodehydration process was accompanied by a competitive reverse-aldol type of degradation

[1] Hough and Taylor, *J.*, 1956, 970.
[2] Hough and Shute, *J.*, 1962, 4633.
[3] Nef, *Annalen*, 1894, **280**, 263.
[4] Hough and Taylor, *J.*, 1955, 3944.
[5] Barker and MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 2297.

to D-galactose (III) and diethylsulphonylmethane, the rate of degradation being dependent upon the pH of the solution. At 60°, the optimum yield of cyclic sulphone was obtained at *ca.* pH 3·5, whereas at pH 7 and above the hexahydroxyheptanes (I) and (II) were completely degraded to D-galactose (III) within 1 hr.; formation of this hexose was also considerable at pH 1.

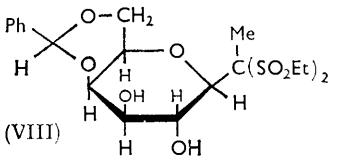
The major component formed on heating the acyclic sulphones (I) and (II) in aqueous solutions at pH 3·5 and 50—60° was isolated by fractionation [2] on a column of anion-exchange resin (Cl^- form; 200 mesh) with water as eluent. In common with the properties of diethylsulphonylglycopyranosylmethanes, the syrupy product was acidic, underwent slow degradation in aqueous ammonia to D-galactose (III) and diethylsulphonylmethane (complete in 5—6 days), and after the initial consumption of 2 mol. of sodium metaperiodate was significantly over-oxidised.[6,7] Acetylation gave a crystalline tetra-acetate (Vb), thus confirming the cyclic structure. Over-oxidation of pyranosylmethanes by periodate has been eliminated by replacement of the acidic hydrogen, in this case at C-β, by a methyl group.[6] Consequently, the *C*-methyl derivative (Vd) was prepared by treating the tetra-acetate (Vb) with silver oxide and methyl iodide, followed by deacetylation by transesterification with sodium methoxide in methanol. The *C*-methyl derivative (Vd) reacted with 2 mol. of periodate to form 1 mol. of formic acid, in accordance with the pyranosyl structure. The titrations of formic acid with alkali showed fading end-points indicative of the presence of formyl esters; [7] titration at 60° gave satisfactory results. The formyl ester (VI) could have arisen by selective cleavage between carbons 3 and 4



by 1 mol. of periodate, followed by cyclic hemiacetal formation between the aldehydo-group at C-3 and primary hydroxyl at C-6, and subsequent oxidative cleavage. As expected, the 4,6-*O*-benzylidene derivative (VIII) reacted with only 1 mol. of periodate, no acidity being produced.

[6] Hough and Richardson, *J.*, 1962, 1019, 1024.
[7] Hough, Taylor, Thomas, and Woods, *J.*, 1958, 1212.

Conformational analysis of the diethylsulphonylpyranosylmethane (Va) favours the chair conformation with the large diethylsulphonylmethane group in the equatorial β-position (IX). Application of Hudson's isorotation rules to the pyranosylmethane ($[M]_D$ +1450°), using methyl α- and β-D-galactopyranosides to determine the ring contribution (B = +18,650°), gave an A value of −17,200° for the anomeric carbon, in agreement with the predicted β-configuration. The formation of the β-pyranosylmethane (Va) as the main product from both epimeric acylic disulphones (I) and (II) lends further support to the accepted postulate that the reaction proceeds through the 1,1-diethylsulphonylpolyhydroxyalk-1-ene (IV), thus destroying the asymmetry at C-2 prior to cyclisation and resynthesis of the asymmetric centre in a stereospecific manner, controlled by conformational factors.



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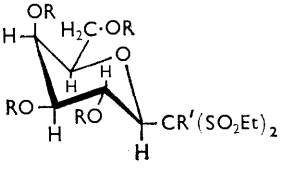


(IX)

Conclusive proof of the β-pyranosyl structure (Vc) was obtained by analysis of the proton magnetic resonance spectra of the tetra-acetate (Vb) and the *C*-methyl derivative (Vc) in chloroform solution. The three equivalent hydrogens of the acetoxy-group give rise to a sharp signal whose chemical shift is characteristic of its geomeric environment.[8] Secondary acetoxy-groups in axial postions resonate at lower field (τ-value) than equatorial groups, which are in turn at lower field than the primary acetates.[9,10] The τ-values of the acetoxymethyl resonances (Table 1) of (Vb) and (Vc) are in agreement with previous values,[9,10] confirm the structures assigned to both compounds, and suggest that they exist in the chair conformation (IX) with one axial ester group.

The assignment of the ring hydrogens and related values of the chemical shifts (Table 1) were facilitated by well resolved multiplets from which the coupling constants were obtained by first-order analysis (Table 2). A triplet with large splitting at τ 4·09 was due

TABLE 1.

Proton chemical shifts (τ-values).

Compound	βH	1H	2H	3H	4H	5H	6H	βMe	2R	3R	4R	6R	$=CH_2$*	$-CH_3$*
(Vb)	5·91	5·44	4·09	4·96	4·60	5·9	5·85	—	7·93;	7·96	7·83	8·01	6·49	8·56
(Vc)	—	5·44	4·05	4·92	4·57	6·04	5·88	8·20	7·94:	7·97	7·83	8·02	6·49	8·52, 8·56

R = methyl of acetoxy-group. * Of the SO_2Et group.

TABLE 2.

Proton coupling constants (c./sec.).

Compound	$J_{\beta,1}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
(Vb)	*ca.* 0·6	9·9	9·3	3·1	<0·5
(Vc)	—	9·1	8·7	3·2	<0·5

to $H_{(2)}$ since this is the only hydrogen flanked by axial hydrogens. Using the values for $J_{1,2}$ and $J_{2,3}$ from the $H_{(2)}$ triplet, the signals due to the hydrogens at positions 1 and 3 were identified. The doublet due to $H_{(1)}$ appeared at τ 5·44 which in (Vb) showed some line-broadening by a small spin-coupling (*ca.* 0·5 c./sec.) with $H_{(\beta)}$ but was absent in the $C_{(\beta)}$-methyl derivative (Vc). As expected, $H_{(3)}$ gave a quartet, at τ 4·96, and, using the derived value for $J_{3,4}$, a doublet at τ 4·60 was attributed to $H_{(4)}$; since the lines of this

[8] Lemieux, Kullnig, Bernstein, and Schneider, *J. Amer. Chem. Soc.*, 1958, **80**, 6098.
[9] Richardson and McLauchlan, *J.*, 1962, 2499.
[10] Sowden, Bowers, Hough, and Shute, *Chem. and Ind.*, 1962, 1851.

TABLE 3.

Approximate dihedral angles.

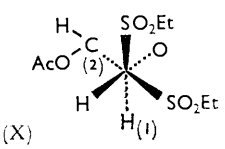
Compound	$\phi_{\beta,1}$	$\phi_{1,2}$	$\phi_{2,3}$	$\phi_{3,4}$	$\phi_{4,5}$
(Vb)	70°	172°	145°	53°	90°
(Vc)	—	145°	143°	52°	90°
Chair conformation (calc.)	—	180°	180°	60°	60°

doublet showed no line-broadening it follows that $J_{4,5} \sim 0$ c./sec. The two $H_{(6)}$ appeared as a doublet which was identified by its intensity; it partially obscured the broad triplet due to $H_{(5)}$ in (Vb) but not in the *C*-methyl derivative (Vc). The $C_{(\beta)}$-methyl peak in (Vc) was clearly seen at τ 8·20 but a singlet for $H_{(\beta)}$ in (Vb) was not resolved. $H_{(\beta)}$ was assumed to lie beneath the high-field part of the $H_{(6)}$ doublet at τ 5·91 since the peaks were unequal in (Vb) but of equal intensity in (Vc).

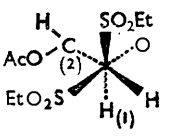
The approximate projected valency angles between the ring hydrogens were calculated (Table 3) from the vicinal proton coupling constants by application of the Karplus equation [11] ($J = J_0 \cos^2\phi - 0{\cdot}28$), using J_0 parameters of 9·27 for $0 \leqslant \phi \leqslant 90°$ and 10·36 for $90° \leqslant \phi \leqslant 180°$, which have given good results for other carbohydrate systems.[12,13] The similarity between the results for (Vb) and (Vc) shows that these derivatives have identical conformations, and the values are close to, but not precisely, those expected for a chair conformation. The β-configuration of the diethylsulphonylmethyl group is confirmed by the dihedral angle of 160—168° found for $H_{(1)}$–$H_{(2)}$; related compounds show high coupling constants for this diaxial relationship. Thus, diethylsulphonyl-(2,3,4-tri-*O*-acetyl-α-D-lyxopyranosyl)methane [13] showed $J_{1,2} = 10{\cdot}4$, and 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl cyanide [14] has $J_{1,2} = 10{\cdot}0$ c./sec. The low value for $J_{4,5}$, also obtained for the latter cyanide,[14] corresponding to a dihedral angle of about 90°, as compared with 60° required for a chair conformation, is difficult to account for since any flattening at this end of the ring, as in a half-chair conformation, to reduce the axial $C_{(4)}$–acetoxyl interactions, decreases $\phi_{4,5}$ to less than 60°. The estimation of $\phi_{4,5}$ cannot be at all accurate (±10%), as it occurs at the change-over in J_0 parameters and the value of $J_{4,5}$ is difficult to determine because it is small.

The use of empirical parameters to adjust the theoretical Karplus formula for closely related series of compounds, such as furanosides [12] and pyranosides,[13] has given reliable and consistent results but the above value obtained in the D-*galacto*-series for $\phi_{4,5}$, an equatorial–axial interaction, emphasises the need for caution.[15]

The proton resonances of the diethylsulphonylmethyl side-chain were also of interest. If there were completely free rotation about the C-β–C-1 bond in (Vb), the coupling constant, $J_{\beta,1}$ would be time-averaged and would thus represent the arithmetic mean of the couplings corresponding to each of the rotamers (X), (XI), and (XII). On this basis, $J_{\beta,1}$ should be $(J_{180°} + 2J_{60°})/3 = 4{\cdot}8$ c./sec. However, the experimentally observed value is approximately 0·6, and this implies that rotation about the C-β–C-1 bond is highly restricted and that the population of rotamer (XII) is very much smaller than that of



(X)



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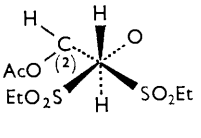

(XII)

either (X) or (XI). The most favourable orientation is shown in (X) since the non-bonded interactions between the acetyl substituent at C-2 and the ethylsulphonyl group at C-β

[11] Karplus, *J. Chem. Phys.*, 1959, **30**, 11.
[12] Abraham, Hall, Hough, and McLauchlan, *J.*, 1962, 3699.
[13] Hall, Hough, McLauchlan, and Pachler, *Chem. and Ind.*, 1962, 1465.
[14] Coxon and Fletcher, *Chem. and Ind.*, 1964, 662.
[15] Karplus, *J. Amer. Chem. Soc.*, 1963, 2870.

will be less than in (XI). A dihedral angle of *ca.* 65° was found for $\phi_{\alpha,1}$ in 2,3,4-tri-*O*-acetyl-diethylsulphonyl-α-D-arabinopyranosylmethane.[13] Whereas the parent compound (Vb) showed conformationally equivalent ethyl groups, the introduction of the $C_{(\beta)}$-methyl substituent altered the situation because the methyl protons of each ethylsulphonyloxy-group now gave two distinct triplets, at 8·52 and 8·56.

Experimental

Melting points were determined on a Kofler hot-stage apparatus. Evaporations were under reduced pressure. Paper chromatography was carried out by the descending method at 21° on Whatman No. 1 filter paper using butan-1-ol–ethanol–water (40 : 11 : 19 v/v) as mobile phase. The compounds were detected with 4% w/v ammoniacal silver nitrate, and rates of movement are quoted relative to the solvent front (R_F). Optical rotations were determined at 24° ± 1° and, unless otherwise stated, in water. The proton magnetic resonance spectra were recorded on a Varian 60 Mc./sec. 4200B spectrometer at ~25°; calibration was by the side-band technique with tetramethylsilane as internal reference.

D-glycero-L-manno-*Heptose*.—1-Deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol monohydrate (15 g.) was dissolved in N-sodium hydroxide (75 ml.) and added slowly to a mixture of concentrated sulphuric acid (9 ml.) in water (12 ml.) at 0°. After standing for 30 min. at room temperature, the solution was neutralised with barium carbonate, filtered, and deionised with Amberlite IR-120(H^+) and IR-45(OH^-) resins. Concentration yielded 12·3 g. of syrupy heptose, R_F 0·14, containing traces of starting material (R_F 0·27) and having $[\alpha]_D$ −13·9° (*c* 2·1) (Found: C, 37·25; H, 7·35. Calc. for $C_7H_{14}O_7,H_2O$; C, 37·85; H, 7·0%). The derived phenylhydrazone had m. p. 192—193° (lit.,[16] 191—192°) (Found: N, 19·7. Calc. for $C_{13}H_{20}N_2O_6$: N, 19·3%).

D-glycero-L-gluco-*Heptose*.[16,17]—1-Deoxy-1-nitro-D-*glycero*-L-*gluco*-heptitol (4 g.) was treated as above. Deionisation and concentration gave a pale green syrup, R_F 0·09, which crystallised on standing (2·5 g., 70%), m. p. 198—199° (from ethanol) (lit.,[16] 198—199°), $[\alpha]_D$ −21 ⟶ −51·9° (*c* 2·0) (Found: C, 39·85; H, 6·85. Calc. for $C_7H_{14}O_7$: C, 40·0; H, 6·65%).

D-glycero-L-manno-*Heptose Diethyl Dithioacetal*.—D-*glycero*-L-*manno*-Heptose (12·3 g.) was shaken with concentrated hydrochloric acid (25 ml.) and ethanethiol (25 ml.) until the product separated from solution. After standing for ½ hr. with occasional shaking, ice–water (50 ml.) was added, and the product was filtered off, washed with water until acid-free, dried, and washed with ether to remove traces of ethanethiol. The crystals (13·6 g., 74%) had m. p. 205—206° (lit.,[18] 204—205°) and R_F 0·72 (Found: C, 41·85; H, 7·95. Calc. for $C_{11}H_{24}O_6S_2$: C, 41·8; H, 7·5%).

D-glycero-L-gluco-*Heptose Diethyl Dithioacetal*.—D-*glycero*-L-*gluco*-Heptose (4·9 g.) was shaken with concentrated hydrochloric acid (10 ml.) and ethanethiol (10 ml.) until the product separated. After standing for ½ hr. with occasional shaking, the product was redissolved in ethanol and the solution neutralised with a slurry of lead carbonate in ethanol. After filtration, the solution was evaporated down to crystals. Recrystallisation from methanol gave the dithioacetal (5·2 g., 70%), m. p. 135—136° (lit.,[17] 133°), $[\alpha]_D$ +5·3° (*c* 2·0 in methanol), R_F 0·68 (Found: C, 41·8; H, 7·8%).

1,1-*Diethylsulphonyl*-D-glycero-L-manno-2,3,4,5,7-*hexahydroxyheptane*.—D-*glycero*-L-*manno*-Heptose diethyl dithioacetal (5 g.) was slurried in a little methanol and treated with an excess of peroxypropionic acid at −10°. The cooled mixture was shaken intermittently for 1 hr.; crystals of the disulphone, which were gradually precipitated, were filtered off. Concentration of the filtrate yielded more crystals. After washing with methanol, the product (4·8 g., 80%), R_F 0·34, was recrystallised from ethanol and had m. p. 173—174° (Found: C, 35·0; H, 6·4; S, 16·2. Calc. for $C_{11}H_{24}O_{10}S_2$: C, 34·7; H, 6·3; S, 16·8%). When the sulphone was dissolved in dilute ammonia, complete degradation to D-galactose occurred within ½ hr. It could not be recrystallised from water without degradation and cyclisation; a paper chromatogram of the aqueous solution showed components at R_F 0·14 (galactose), 0·33 (acyclic disulphone), and 0·56 (cyclic disulphone).

[16] Sowden and Strobach, *J. Amer. Chem. Soc.*, 1960, **82**, 954.
[17] Hann and Hudson, *J. Amer. Chem. Soc.*, 1934, **56**, 2080; 1937, **59**, 548.
[18] Hann and Hudson, *J. Amer. Chem. Soc.*, 1937, **59**, 1898.

1,1-*Diethylsulphonyl*-D-glycero-L-gluco-2,3,4,5,6,7-*hexahydroxyheptane*.—D-*glycero*-L-*gluco*-Heptose diethyl dithioacetal (3·5 g.) was slurried in dioxan and treated with an excess of peroxypropionic acid at −10°. After standing for 2 hr., the solution was concentrated to a gel which, after evaporation several times with ethanol, gave crystals (1·25 g.) and a residual syrup (3 g.). Both crystals and syrup were shown to contain two components, R_F 0·37 and 0·56. Recrystallisation of the crystals several times from ethanol yielded the chromatographically pure *product*, R_F 0·37, m. p. 120—170° (Found: C, 34·9; H, 6·2%). The product was very water-soluble, the aqueous solution showing two components on a paper chromatogram (R_F 0·37, 0·56). Degradation in dilute ammonia was complete within ½ hr.

Cyclisation of the Aldoheptose Disulphones, and Separation of the Products.—Samples of the D-*glycero*-L-*manno*-disulphone were warmed at *ca.* 60° in aqueous acetic acid at pH 5, 4, 3, and 2, in hydrochloric acid at pH 1, and in phosphate buffer at pH 7. After 6 hr., paper chromatography indicated the complete absence of the straight-chain disulphone and the appearance of four components having R_F 0·14 (galactose), 0·23, 0·48, and 0·54. The sample in hydrochloric acid had been degraded considerably to galactose. The four samples in acetic acid gave similar results to each other; the two slowest components were very faint, the next (R_F 0·48) somewhat stronger, and the fastest (R_F 0·54) by far the strongest. The sample in buffered solution (pH 7) had been degraded completely to galactose after warming at 60° for 1 hr.

1,1-Diethylsulphonyl-D-*glycero*-L-*manno*-2,3,4,5,6,7-hexahydroxyheptane (9 g.) was warmed in aqueous acetic acid (250 ml.; pH 3·5) at 50—60° until all the starting material had reacted. The solution was concentrated several times with ethanol and finally evaporated to dryness, yielding a colourless syrup containing components having R_F 0·15, 0·23 (very weak), 0·48 (weak), and 0·54 (strong).

The D-*glycero*-L-*gluco*-disulphone (0·3 g.) was warmed in aqueous solution for a few minutes. Concentration gave a syrup which paper chromatography showed to have the same composition as above.

The syrup (5 g.) was dissolved in a little water, run on to a column of Deacidite FF anion-exchange resin (Cl^- form) and eluted with water at a rate of 15—20 ml./hr. After examination of the eluate on paper chromatograms it was grouped into six main fractions: 1 (0·1 g.), R_F 0·15 (galactose, strong) and 0·23 (weak); 2 (0·21 g.), R_F 0·15, 0·23 (traces), and 0·48 (strong), $[\alpha]_D$ +17°; 3 (0·23 g.), R_F 0·48, 0·55 (both strong); 4 (2 g.), R_F 0·55, $[\alpha]_D$ +4° (*c* 2·0 in acetone); 5 (0·3 g.), R_F 0·55 (strong), 0·70 (weak); 6 (0·1 g.), diethylsulphonylmethane, R_F 0·72, m. p. and mixed m. p. 101—102°, $[\alpha]_D$ 0°.

2,3,4,6-*Tetra*-O-*acetyldiethylsulphonyl*-β-D-*galactopyranosylmethane*.—The syrupy disulphone (1 g.) was heated at 95—100° for 20 min. with acetic anhydride (10 ml.) and concentrated sulphuric acid (2 drops). After neutralisation with saturated sodium hydrogen carbonate and extraction of the product with chloroform, concentration of the extract to dryness yielded a syrup which crystallised on standing. After recrystallisation twice from ethanol–light petroleum, the *acetate* (1·3 g., 89%) had m. p. 149—150°, $[\alpha]_D$ +11·5° (*c* 2·0 in acetone) (Found: C, 43·3; H, 5·8. $C_{19}H_{30}O_{13}S_2$ requires C, 43·0; H, 5·65%).

1,1-*Diethylsulphonyl*-1-(2,3,4,6-*tetra*-O-*acetyl*-β-D-*galactopyranosyl*)*ethane*.—The tetra-acetate (1·3 g.) was boiled under reflux in methyl iodide (10 ml.) in the presence of silver oxide (3 g.), which was added in three portions at intervals of 1 hr. The solution was filtered and the solids washed well with acetone. The filtrate and washings were concentrated to a pale orange syrup which crystallised on standing. The crystals were redissolved in ethanol (charcoal) and the solution concentrated to a small volume. Addition of light petroleum precipitated needle-like crystals of the C-*methyl derivative*, m. p. 151—153° (from ethanol–light petroleum) (1·0 g., 75%), mixed m. p. with the starting material *ca.* 120°, $[\alpha]_D$ +11·0° (*c* 2·0 in acetone) (Found: C, 44·0; H, 5·95. $C_{20}H_{32}O_{13}S_2$ requires C, 44·1; H, 5·9%).

The crystals (0·8 g.) were treated with 12% w/v sodium methoxide in methanol (5 ml.) for 4 hr. Deionisation with Amberlite IR-120(H^+) and IR-45(OH^-) resins, followed by concentration, yielded a colourless syrup which gave a cloudy solution in water. Filtration through Hyflo Supercell, and concentration, gave a hygroscopic syrup (0·3 g., 60%) of 1,1-*diethylsulphonyl*-1-(β-D-*galactopyranosyl*)*ethane*, R_F 0·56, $[\alpha]_D$ +3·5° (*c* 1·62 in acetone) (Found: C, 37·95; H, 6·75. $C_{12}H_{24}O_9S_2$ requires C, 38·3; H, 6·4%).

1,1-*Diethylsulphonyl*-1-(4,6-O-*benzylidene*-β-D-*galactopyranosyl*)*ethane*.—The cyclic *C*-methyl-disulphone (0·18 g.) was treated with 98—100% formic acid (10 ml.) and benzaldehyde (10 ml.). After 5 min. the solution was poured into light petroleum (b. p. 60—80°) (15 ml.) and water

(15 ml.) containing potassium carbonate (5 g.). The oily product which separated between the two layers was isolated, and washed with light petroleum until it no longer smelt of benzaldehyde. The resultant orange syrup was dissolved in methanol (charcoal), and concentrated to a colourless syrup which, on standing, gave an amorphous solid, m. p. 78—100°, $[\alpha]_D$ −22·2° (*c* 2·12 in acetone). Addition of any solvent turned the solid into syrup (Found: C, 48·35; H, 6·1. $C_{19}H_{28}O_9S_2$ requires C, 49·15; H, 6·05%).

Periodate Oxidations.—A solution of the carbohydrate derivative (*ca.* 0·01M) in 0·015M-sodium metaperiodate was kept in the dark at room temperature. At various intervals, aliquot portions (10 ml.) were removed from the reaction mixture and a suitable control for the determinations of periodate uptake and formic acid liberated.[7] The results were as follows:

(a) Diethylsulphonyl-β-D-galactopyranosylmethane (0·0014M).

Time (hr.)	0·25	1	2	4	9	19	44
Periodate uptake (mol.)	0·75	1·28	1·49	1·70	1·89	2·18	2·66
Formic acid (mol.)	0·38	0·59	0·79	0·99	1·22	1·53	2·00

(b) 1,1-Diethylsulphonyl-1-(β-D-galactopyranosyl)ethane (0·0014M).

Time (hr.)	1	4	8	18
Periodate uptake (mol.)	1·53	1·82	1·99	1·98
Formic acid * (mol.)	0·24	0·55	0·91	1·00

* The titrations were carried out at *ca.* 60° in order to avoid fading end-points.

(c) 1,1-Diethylsulphonyl-1-(4,6-*O*-benzylidene-β-D-galactopyranosyl)ethane (0·0009M).

Time (hr.)	1	3	7	24
Periodate uptake (mol.)	0·61	0·97	1·01	0·99

No formic acid was produced

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