211. *Some Carbohydrate Episulphides.*

By A. M. Creighton and L. N. Owen.

Syntheses are described of some episulphides related to L-iditol, L-gulitol, and L-idose; these represent a new type of carbohydrate derivative. Thiols are formed by reductive fission of these episulphides, whilst by reaction with xanthate they furnish known, but previously incorrectly formulated, trithiocarbonates.

Although epoxides are well known in carbohydrate chemistry, where they have played important synthetical rôles, the corresponding episulphides have apparently not been reported. Since such compounds should show interesting and useful properties, and could probably act as intermediates in syntheses of thio-sugars and deoxy-sugars, we have carried out some exploratory investigations in this field.

It is known [1] that the primary tosyl group in 1,3:2,4-di-*O*-ethylidene-5,6-di-*O*-tosyl-D-glucitol (I) reacts readily with potassium thiolacetate and gives 6-acetylthio-6-deoxy-1,3:2,4-di-*O*-ethylidene-5-*O*-tosyl-D-glucitol (II). Such a compound is an obvious source of a terminal episulphide, and on treatment with base it gave an excellent yield of 5,6-dideoxy-5,6-epithio-1,3:2,4-di-*O*-ethylidene-L-iditol (III), the configuration being based on the inversion at $C_{(5)}$ which must occur when it is attacked by the neighbouring thiol anion. Desulphurisation of the episulphide with Raney nickel gave the known [2] 5,6-dideoxy-1,3:2,4-di-*O*-ethylidene-D-glucitol (X).

Reaction of 1,2:3,4-di-*O*-isopropylidene-5,6-di-*O*-tosyl-D-mannitol [2] (V) with potassium thiolacetate followed a course similar to that observed [1] in the D-glucitol series and gave 6-acetylthio-6-deoxy-1,2:3,4-di-*O*-isopropylidene-5-*O*-tosyl-D-mannitol (VI), which with base furnished 5,6-dideoxy-5,6-epithio-1,2:3,4-di-*O*-isopropylidene-L-gulitol (VII). Similarly, 3-*O*-acetyl-1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-glucose [3] gave successively 3-*O*-acetyl-6-acetylthio-6-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-glucose (XIX) and 5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-L-idose (XX).

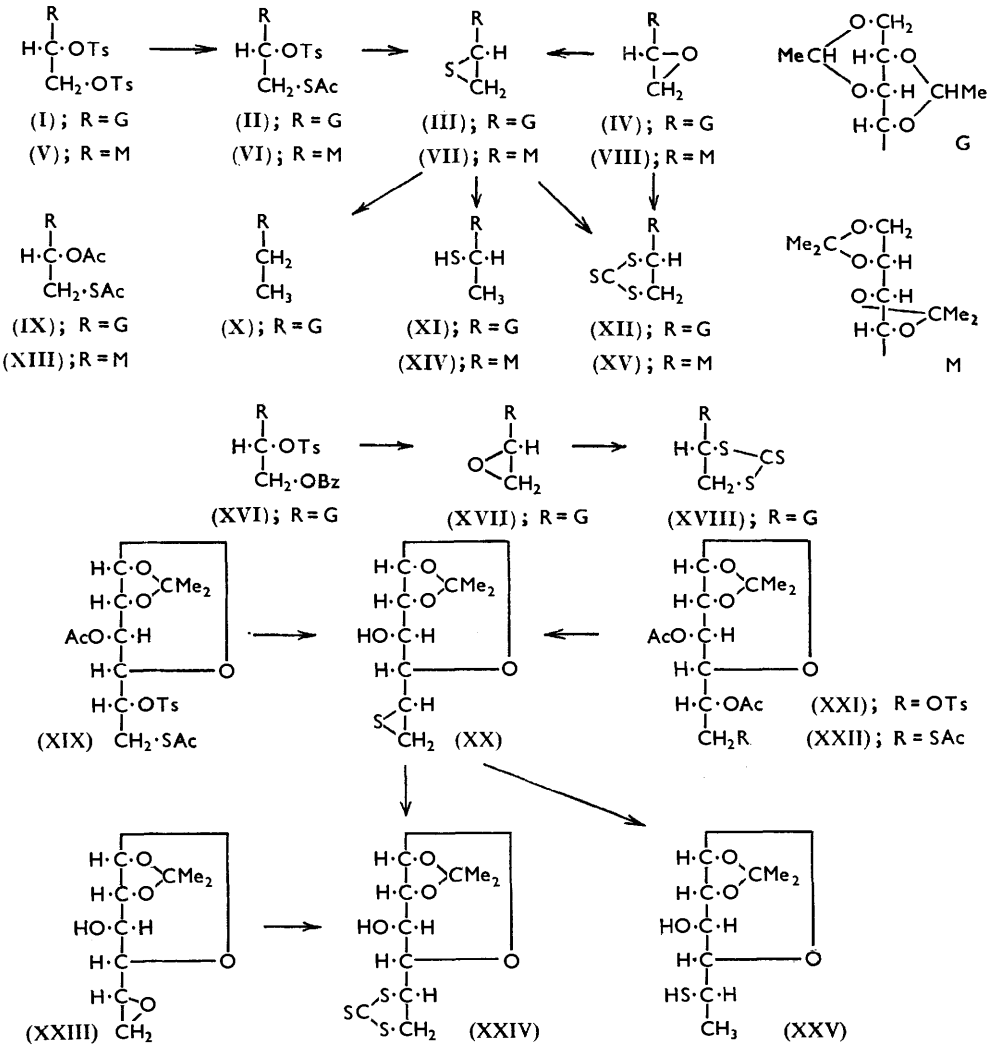
A recognised method [4] for the preparation of episulphides is the reaction of an epoxide with thiourea or an alkali-metal thiocyanate. Application of this procedure to 5,6-anhydro-1,3:2,4-di-*O*-ethylidene-D-glucitol (IV),[5] thiourea being used under Bordwell and Andersen's modified conditions,[4g] gave the episulphide (III) identical with that obtained from the thiolacetate (II); this result is in agreement with the mechanism of the reaction,[4e-g,6] which when stereoisomerism is possible leads to the episulphide of opposite configuration. The yield by this route was, however, much lower than that obtained from the thiolacetate.

The alkaline hydrolysis of acetylated vicinal hydroxy-thiols is often accompanied by cyclisation to give episulphides,[7,8] the extent to which this occurs being greatly influenced by structural factors. In some cases [7,9] the reaction is of preparative value, and it was therefore of interest to discover whether it could be usefully applied to the synthesis of carbohydrate episulphides. 3,5-Di-*O*-acetyl-6-acetylthio-6-deoxy-1,2-*O*-isopropylidene-α-D-glucose (XXII), conveniently synthesised from the known toluene-*p*-sulphonate (XXI),[3]

[1] Chapman and Owen, *J.*, 1950, 579.
[2] Bladon and Owen, *J.*, 1950, 598.
[3] Ohle, Euler, and Lichtenstein, *Ber.*, 1929, **62**, 2885.
[4] (*a*) Dachlauer and Jackel, G.P. 636,708/1936; (*b*) Culvenor, Davies, and Pausacker, *J.*, 1946, 1050; (*c*) Snyder, Stewart, and Ziegler, *J. Amer. Chem. Soc.*, 1947, **69**, 2672; (*d*) Culvenor, Davies, and Heath, *J.*, 1949, 278; (*e*) van Tamelen, *J. Amer. Chem. Soc.*, 1951, **73**, 3444; (*f*) Price and Kirk, *ibid.*, 1953, **75**, 2396; (*g*) Bordwell and Andersen, *ibid.*, p. 4959.
[5] Vargha and Puskás, *Ber.*, 1943, **76**, 859.
[6] Culvenor, Davies, and Savige, *J.*, 1952, 4480.
[7] Miles and Owen, *J.*, 1952, 817.
[8] Harding and Owen, *J.*, 1954, 1528; Fitt and Owen, *J.*, 1957, 2240.
[9] Goodman, Benitez, and Baker, *J. Amer. Chem. Soc.*, 1958, **80**, 1680.

was treated with sodium methoxide in chloroform–methanol, but although the episulphide (XX) was readily isolated the yield was only 10%; consequently the analogous hexitol derivatives (IX) and (XIII), each of which was synthesised by ring-fission of the appropriate 5,6-epoxide (IV) [5] or (VIII) [10] with thiolacetic acid, followed by acetylation, were not further examined.

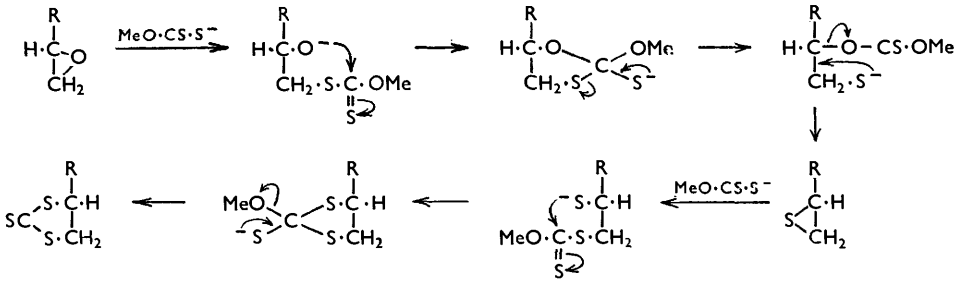
The three episulphides (III), (VII), and (XX) appear to be stable, and show no change in properties after storage for two years. Each, on reduction with lithium aluminium hydride, afforded the respective 5,6-dideoxy-5-mercapto-compound (XI), (XIV), or (XXV),



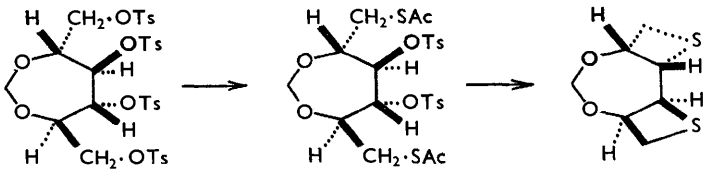
ring-fission being assumed to occur, as with terminal aliphatic episulphides,[11] at the primary position. Each episulphide, on reaction with potassium methyl xanthate,[4b] gave a crystalline trithiocarbonate which, attack at the primary position again being

[10] Bladon and Owen, *J.*, 1950, 591.
[11] Bordwell, Anderson, and Pitt, *J. Amer. Chem. Soc.*, 1954, **76**, 1082.

assumed,[4c,12] must have the same configuration at $C_{(5)}$ as the episulphide from which it was derived. These products are therefore 5,6-dideoxy-1,3:2,4-di-*O*-ethylidene-5,6-(thiocarbonyldithio)-L-iditol (XII), 5,6-dideoxy-1,2:3,4-di-*O*-isopropylidene-5,6-(thiocarbonyldithio)-L-gulitol (XV), and 5,6-dideoxy-1,2-*O*-isopropylidene-5,6-(thiocarbonyldithio)-α-L-idose (XXIV). McSweeney and Wiggins[13] briefly reported the formation of trithiocarbonates by the action of potassium methyl xanthate on each of the 5,6-anhydro-compounds (IV), (VIII), and (XXIII), but they assigned to them the same configurations as the original epoxides. This, however, cannot be so, because the reaction of an epoxide with xanthate involves the formation, as an intermediate, of an episulphide of opposite configuration at the carbon atoms concerned, and if this is a terminal episulphide the altered configuration is retained in the trithiocarbonate; the complete mechanistic sequence can thus be formulated as shown.



In accordance with this scheme, we find that the trithiocarbonates prepared from these epoxides are respectively identical with (XII), (XV), and (XXIV) prepared from our episulphides. Furthermore, a different trithiocarbonate (XVIII) was obtained by the action of xanthate on 5,6-anhydro-1,3:2,4-di-*O*-ethylidene-L-iditol (XVII), synthesised from the known[14] 6-*O*-benzoyl-1,3:2,4-di-*O*-ethylidene-5-*O*-tosyl-D-glucitol (XVI). The reductive fission of trithiocarbonates to give dithiols is described in the following paper.



(XXVI) (XXVII) (XXVIII)

The formation of a trimethylene sulphide ring, by displacement of a toluene-*p*-sulphonyloxy-group by a suitably placed thiol anion, has been encountered[15] in the pentaerythritol series. This reaction has now been applied to 1,6-diacetylthio-1,6-dideoxy-2,5-*O*-methylene-3,4-di-*O*-tosyl-D-mannitol (XXVII) [prepared by selective replacement of the primary groups in the tetra-*O*-tosyl compound (XXVI)[16]], which on treatment with base gave a crystalline product, presumably 1,3,4,6-tetradeoxy-1,3:4,6-diepithio-2,5-*O*-methylene-D-iditol (XXVIII), since the methylene bridge renders impossible the alternative 1,4:3,6-diepithio-structure. Although Baker[17] has claimed to have prepared

[12] Cf. Davies and Savige, *J.*, 1950, 317; 1951, 774.
[13] McSweeney and Wiggins, *Nature*, 1951, **168**, 874.
[14] Matheson and Angyal, *J.*, 1952, 1133.
[15] Bladon and Owen, *J.*, 1950, 585.
[16] Ness, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1943, **65**, 2215.
[17] Baker, *Canad. J. Chem.*, 1953, **31**, 821.

1,4:3,6-dianhydro-2,5-*O*-methylene-D-iditol, his product was almost certainly the 1,3:4,6-dianhydro-compound; his isolation of 1,4:3,6-dianhydro-D-iditol after acid hydrolysis could be explained by rearrangement to the more stable system after removal of the restrictive methylene bridge.

Experimental

Microanalyses were by Miss J. Cuckney and the staff of the Organic Chemistry Microanalytical Laboratories. Absorption spectra, recorded in ethanol for the ultraviolet and in carbon disulphide for the infrared region, were by Mr. R. L. Erskine, B.Sc., A.R.C.S., and Mrs. A. I. Boston. Optical rotations were determined in chloroform.

5-O-*Acetyl*-6-*acetylthio*-6-*deoxy*-1,3:2,4-*di*-O-*ethylidene*-D-*glucitol* (IX).—A solution of 5,6-anhydro-1,3:2,4-di-*O*-ethylidene-D-glucitol [5] (1·0 g.) in thiolacetic acid (3 c.c.) was boiled under reflux for 1½ hr. and then distilled. The lower-boiling fractions, which contained excess of acid and some unchanged epoxide, were followed by an oil (0·16 g.), b. p. 100°/0·005 mm., which after acetylation (pyridine–acetic anhydride) gave the *compound* (IX), m. p. 113° (from ethanol) (Found: C, 50·2; H, 6·8; S, 9·5. $C_{14}H_{22}O_7S$ requires C, 50·3; H, 6·6; S, 9·6%); $\lambda_{max.}$ 230 mμ (ε 4300).

5-O-*Acetyl*-6-*acetylthio*-6-*deoxy*-1,2:3,4-*di*-O-*isopropylidene*-D-*mannitol* (XIII).—A solution of 5,6-anhydro-1,2:3,4-di-*O*-isopropylidene-D-mannitol [10] (1·0 g.) in thiolacetic acid (3 c.c.) was boiled under reflux for 6 hr. and then distilled. The main fraction (0·7 g.), b. p. 115—125°/0·002 mm., on acetylation gave the *compound* (XIII), m. p. 67—68° (from methanol) (Found: C, 53·0; H, 7·4; S, 8·8. $C_{16}H_{26}O_7S$ requires C, 53·0; H, 7·2; S, 8·9%); $\lambda_{max.}$ 230 mμ (ε 3350).

3,5-*Di*-O-*acetyl*-6-*acetylthio*-6-*deoxy*-1,2-O-*isopropylidene*-α-D-*glucose* (XXII).—A mixture of 3,5-di-*O*-acetyl-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-glucose [3] (5·6 g.), potassium thiolacetate (1·7 g.), and acetone (100 c.c.) was boiled under reflux for 7 hr., then cooled, filtered, concentrated, and diluted with water. Recrystallisation of the precipitate from methanol gave needles (1·6 g.), m. p. 86—87°, of the *compound* (XXII); further recrystallisation from light petroleum (b. p. 40—60°) raised the m. p. to 88—89°; $[\alpha]_D^{20}$ +38° (*c* 4) (Found: C, 49·9; H, 6·4; S, 8·7. Calc. for $C_{15}H_{22}O_8S$: C, 49·7; H, 6·1; S, 8·9%); $\lambda_{max.}$ 229 mμ (ε 3900). Ohle and Mertens [18] report m. p. 69°, $[\alpha]_D^{18}$ +44° (*c* 3 in chloroform).

6-*Acetylthio*-6-*deoxy*-1,2:3,4-*di*-O-*isopropylidene*-5-O-*tosyl*-D-*mannitol* (VI).—A mixture of 1,2:3,4-di-*O*-isopropylidene-5,6-di-*O*-tosyl-D-mannitol * (29 g.), potassium thiolacetate (6·3 g.), and acetone (250 c.c.) was boiled under reflux for 6 hr., then filtered and concentrated. The residue was diluted with ether, and the solution washed with water, dried (Na_2SO_4), and evaporated to a solid, which on recrystallisation from methanol gave the *compound* (VI) (14·5 g., 60%), m. p. 74—75°, raised on further recrystallisation to 76—77° (Found: C, 53·2; H, 6·5; S, 13·5. $C_{21}H_{30}O_8S_2$ requires C, 53·2; H, 6·4; S, 13·5%); $\lambda_{max.}$ 228 and 262 mμ (ε 13200 and 550).

3-O-*Acetyl*-6-*acetylthio*-6-*deoxy*-1,2-O-*isopropylidene*-5-O-*tosyl*-α-D-*glucose* (XIX).—Similar treatment of 3-*O*-acetyl-1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-glucose [3] (10·3 g.) with potassium thiolacetate (2·3 g.) in boiling acetone (125 c.c.), but with chloroform for the working-up, gave the *compound* (XIX) (7·8 g., 91%), m. p. 131—133° (from ethanol) (Found: C, 50·7; H, 5·8; S, 13·6. $C_{20}H_{26}O_9S_2$ requires C, 50·6; H, 5·5; S, 13·5%); $\lambda_{max.}$ 226 and 262 mμ (ε 13,800 and 665).

5,6-*Dideoxy*-5,6-*epithio*-1,3:2,4-*di*-O-*ethylidene*-L-*iditol* (III).—(i) Methanolic sodium methoxide [from sodium (1·0 g.) and dry methanol (40 c.c.)] was added at 0° to a stirred solution of 6-acetylthio-6-deoxy-1,3:2,4-di-*O*-ethylidene-5-*O*-tosyl-D-glucitol [1] (20 g.) in chloroform (150 c.c.). The resulting gel was vigorously stirred for 10 min., then neutralised with carbon dioxide and quickly washed with water. Evaporation of the dried (Na_2SO_4) chloroform solution, and recrystallisation of the product from ethanol, gave large needles (9·5 g., 89%) of the *episulphide* (III), m. p. 150—151°, $[\alpha]_D^{23}$ +3° (*c* 5) (Found: C, 51·8; H, 7·0; S, 13·9. $C_{10}H_{16}O_4S$ requires C, 51·7; H, 6·9; S, 13·8%); $\lambda_{max.}$ 257 mμ (ε 60); $\nu_{max.}$ 666, 672, 801, 816, 887, 945, 952, 1037, and 1057 cm.$^{-1}$.

(ii) A solution of 5,6-anhydro-1,3:2,4-di-*O*-ethylidene-D-glucitol [5] (2·2 g.) and thiourea

* Prepared by Bladon and Owen's method,[2] but with a reaction time of 3 days at room temperature.

[18] Ohle and Mertens, *Ber.*, 1935, **68**, 2176.

(0·76 g.) in dioxan (25 c.c.) containing sulphuric acid (0·01 g.) was boiled under reflux for 7 hr., then concentrated, diluted with chloroform, and washed with water. Evaporation of the dried solution left an oil, which when heated at 0·001 mm. gave a sublimate (0·7 g.), m. p. 121—128°. Two recrystallisations from ethanol gave the above episulphide, m. p. and mixed m. p. 150—151°, $[\alpha]_D^{20}$ +3·3° (*c* 5).

Desulphurisation. The episulphide (1·0 g.) and Raney nickel (*ca.* 8 g.) were boiled under reflux in ethanol (25 c.c.) for 3 hr. Filtration and evaporation gave a solid (0·8 g.) which was recrystallised from light petroleum (b. p. 60—80°), giving needles of 5,6-dideoxy-1,3:2,4-di-*O*-ethylidene-D-glucitol, m. p. and mixed [2] m. p. 85°.

5,6-*Dideoxy*-5,6-*epithio*-1,2:3,4-di-O-*isopropylidene*-L-*gulitol* (VII).—Reaction of 6-acetylthio-6-deoxy-1,2:3,4-di-*O*-isopropylidene-5-*O*-tosyl-D-mannitol (18·5 g.) in chloroform (200 c.c.) with sodium methoxide [from sodium (0·91 g.) and methanol (38 c.c.)], at 0°, followed by isolation as for (III), gave the *episulphide* (VII) (7·6 g., 72%), b. p. 90—92°/0·01 mm., n_D^{21} 1·4790, $[\alpha]_D^{23}$ +30° (*c* 1) (Found: C, 55·4; H, 7·8; S, 12·3. $C_{12}H_{20}O_4S$ requires C, 55·4; H, 7·8; S, 12·3%); $\lambda_{max.}$ 275 mμ (ε 74); $\nu_{max.}$ 664, 796, 815, 893, 962, 1043, and 1072 cm.$^{-1}$.

5,6-*Dideoxy*-5,6-*epithio*-1,2-O-*isopropylidene*-α-L-*idose* (XX).—(i) Reaction of 3-*O*-acetyl-6-acetylthio-6-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-glucose (5·5 g.), in chloroform (60 c.c.) with sodium methoxide [from sodium (0·26 g.) and methanol (11 c.c.)], initially at −30°, but with the temperature rising to 0° in 30 min., gave, after isolation as for (III), the episulphide (XX) (1·85 g., 73%) which after recrystallisation from methanol and then from carbon tetrachloride formed long needles, m. p. 164—165°, $[\alpha]_D^{23}$ −16° (*c* 5) (Found: C, 49·5; H, 6·7; S, 14·5. $C_9H_{14}O_4S$ requires C, 49·5; H, 6·5; S, 14·7%); $\lambda_{max.}$ 258 mμ (ε 48); $\nu_{max.}$ 672, 816, 887, 944, 958, 1040, 1053, and 1060 cm.$^{-1}$.

(ii) 5N-Methanolic potassium hydroxide (1·0 c.c.) was added to a solution of 3,5-di-*O*-acetyl-6-acetylthio-6-deoxy-1,2-*O*-isopropylidene-α-D-glucose (0·65 g.) in chloroform (5 c.c.) at −10°. The temperature was allowed to rise to 20° during 30 min. and the solution was then quickly washed with N-sodium hydroxide, and then with water, dried (Na_2SO_4), and evaporated to a solid, which on recrystallisation from methanol gave needles (0·04 g., 10%) of the episulphide, m. p. and mixed m. p. 164—165°.

Reduction of the Episulphides with Lithium Aluminium Hydride.—(i) 5,6-Dideoxy-5,6-epithio-1,3:2,4-di-*O*-ethylidene-L-iditol (1·5 g.) and lithium aluminium hydride (1·2 g.) in ether (60 c.c.) were boiled under reflux for 6 hr. The excess of hydride was destroyed with ethyl acetate, and the mixture was then poured into N-acetic acid (420 c.c.) at 0° and quickly extracted with ether. The extracts were washed with aqueous sodium hydrogen carbonate, then dried (Na_2SO_4), and evaporated to give a solid thiol (1·1 g.). Recrystallisation from ethanol–light petroleum (b. p. 40—60°) gave 5,6-*dideoxy*-1,3:2,4-*di*-O-*ethylidene*-5-*mercapto*-L-*iditol* (XI) as stout needles, m. p. 128°, $[\alpha]_D^{22}$ +37° (*c*, 3) (Found: C, 51·5; H, 8·1; S, 13·7; thiol S, 13·8. $C_{10}H_{18}O_4S$ requires C, 51·3; H, 7·8; S, 13·7%).

(ii) 5,6-Dideoxy-5,6-epithio-1,2:3,4-di-*O*-isopropylidene-L-gulitol (5·5 g.) was similarly reduced with lithium aluminium hydride (2·0 g.) in ether (70 c.c.), and gave 5,6-*dideoxy*-1,2:3,4-*di*-O-*isopropylidene*-5-*mercapto*-L-*gulitol* (XIV) (4·9 g.), b. p. 67—68°/0·002 mm., m. p. 48—49°, n_D^{26} 1·4621, $[\alpha]_D^{23}$ +46° (*c* 5) (Found: C, 55·0; H, 8·6; S, 12·1. $C_{12}H_{22}O_4S$ requires C, 55·0; H, 8·5; S, 12·2%).

(iii) 5,6-Dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-L-idose (1·1 g.) in tetrahydrofuran (30 c.c.) was added to lithium aluminium hydride (0·3 g.) in ether (30 c.c.), and the mixture was boiled under reflux for 2 hr. Isolation as above gave 5,6-*dideoxy*-1,2-O-*isopropylidene*-5-*mercapto*-α-L-*idose* (XXV) (0·55 g.), prisms [from ethanol–light petroleum (b. p. 40—60°)], m. p. 93—94°, $[\alpha]_D^{23}$ −24° (*c* 4) (Found: C, 49·2; H, 7·4; thiol S, 14·4. $C_9H_{16}O_4S$ requires C, 49·1; H, 7·3; S, 14·5%).

Trithiocarbonates.—(a) *From episulphides.* (i) 5,6-Dideoxy-5,6-epithio-1,3:2,4-di-*O*-ethylidene-L-iditol (1·16 g.) was dissolved in a solution of potassium hydroxide (1·4 g.) and carbon disulphide (3 c.c.) in methanol (10 c.c.). The mixture was boiled under reflux for 2 hr. and then cooled and diluted with water, giving yellow needles of 5,6-dideoxy-1,3:2,4-di-*O*-ethylidene-5,6-(thiocarbonyldithio)-L-iditol (XII) (1·43 g., 93%), m. p. 182—183° unchanged on recrystallisation from methanol (lit.,[13] m. p. 182—183°).

(ii) Similar treatment of 5,6-dideoxy-5,6-epithio-1,2:3,4-di-*O*-isopropylidene-L-gulitol (0·15 g.) gave yellow needles of 5,6-dideoxy-1,2:3,4-di-*O*-isopropylidene-5,6-(thiocarbonyldithio)-L-gulitol (XV) (0·18 g., 94%), m. p. 95—96° (lit.,[13] m. p. 95—96°).

(iii) Similar treatment of 5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-L-idose (0·14 g.) gave yellow needles of 5,6-dideoxy-1,2-*O*-isopropylidene-5,6-(thiocarbonyldithio)-α-L-idose (XXIV) (0·18 g., 95%), m. p. 179—180° (lit.,[13] m. p. 179·5—180·5°).

(b) *From epoxides.* (i) 5,6-Anhydro-1,3:2,4-di-*O*-ethylidene-D-glucitol [5] (0·29 g.) was treated as above (but under reflux for 4 hr.) with a solution of potassium hydroxide (0·35 g.) and carbon disulphide (1 c.c.) in methanol (8 c.c.), and gave the trithiocarbonate (XII) (0·25 g., 61%) identical (m. p. and mixed m. p. 182—183°) with that described above.

(ii) 5,6-Anhydro-1,2:3,4-di-*O*-isopropylidene-D-mannitol [10] (3·0 g.), with potassium hydroxide (3·0 g.), carbon disulphide (3 c.c.), and methanol (25 c.c.), similarly gave the trithiocarbonate (XV) (2·1 g., 51%), m. p. and mixed m. p. 95—96°.

(iii) 5,6-Anhydro-1,2-*O*-isopropylidene-α-D-glucose [19] (0·1 g.) on similar treatment gave the trithiocarbonate (XXIV) (0·1 g.), m. p. and mixed m. p. 179—180°.

(iv) 6-*O*-Benzoyl-1,3:2,4-di-*O*-ethylidene-5-*O*-tosyl-D-glucitol [14] (1·5 g.) in chloroform (30 c.c.) was treated at −10° with sodium methoxide [from sodium (0·07 g.) and methanol (3 c.c.)]. The temperature was allowed to rise to 20° during 2 hr., and the solution was then washed with water, dried ($MgSO_4$), and evaporated. Crystallisation of the residue from ethanol–light petroleum (b. p. 60—80°) gave hexagonal plates (0·38 g., 61%) of *5,6-anhydro-1,3:2,4-di-O-ethylidene-L-iditol*, m. p. 150—151°, $[\alpha]_D^{21}$ −28° (*c* 7) (Found: C, 55·7; H, 7·7. $C_{10}H_{16}O_5$ requires C, 55·5; H, 7·5%).

This anhydro-compound (0·32 g.) on treatment as above with potassium methyl xanthate gave *5,6-dideoxy-1,3:2,4-di-O-ethylidene-5,6-(thiocarbonyldithio)-D-glucitol* (XVIII) (0·12 g.) as a yellow glass, b. p. 100—110° (bath)/0·005 mm. (Found: C, 43·0; H, 4·9. $C_{11}H_{16}O_4S_3$ requires C, 42·9; H, 5·2%).

1,6-Diacetylthio-1,6-dideoxy-2,5-O-methylene-3,4-di-O-tosyl-D-mannitol (XXVII).—2,5-*O*-Methylene-1,3,4,6-tetra-*O*-tosyl-D-mannitol [16] (16·5 g.), potassium thiolacetate (12 g.), and ethyl methyl ketone (400 c.c.) were boiled under reflux for 4½ hr. The dark red mixture was cooled, poured into water, and extracted with chloroform to give a solid, which on recrystallisation from ethanol gave needles (7·2 g., 57%) of the *bisthiolacetate* (XXVII), m. p. 112°, $[\alpha]_D^{21}$ −30° (*c* 18) (Found: C, 48·7; H, 5·1; S, 20·8. $C_{25}H_{30}O_{10}S_4$ requires C, 48·5; H, 4·9; S, 20·7%); $\lambda_{max.}$ 226 and 262 mμ (ε 34,000 and 1500).

1,3,4,6-Tetradeoxy-1,3:4,6-diepithio-2,5-O-methylene-D-iditol (XXVIII).—To the above bisthiolacetate (XXVII) (1·5 g.) in chloroform (25 c.c.), sodium methoxide [from sodium (0·115 g.) and methanol (4·8 c.c.)] was added at −10°. The mixture was set aside for 4 days, then neutralised with carbon dioxide, washed with water, dried ($MgSO_4$), and evaporated to a solid. Recrystallisation from ethyl acetate–light petroleum (b. p. 40—60°) gave a first crop, m. p. 140—150°, which on further recrystallisation from ethyl acetate gave fine needles (0·11 g.), probably of *di-(4,6-dideoxy-4,6-epithio-2,5-O-methylene-3-O-tosyl-D-talitol) disulphide*, m. p. 162—163° (Found: C, 46·4; H, 5·0; O, 21·9. $C_{28}H_{34}O_{10}S_6$ requires C, 46·5; H, 4·7; O, 22·1%); $\lambda_{max.}$ 262 mμ (ε 1900 in chloroform). Concentration of the combined mother-liquors, and sublimation at 100° (bath)/1 mm. afforded large rhombs of the *diepithio*-compound (XXVIII) (0·12 g.), m. p. 146—147° (Found: C, 44·3; H, 5·2; S, 33·5. $C_7H_{10}O_2S_2$ requires C, 44·2; H, 5·3; S, 33·7%); $\lambda_{max.}$ 260 mμ (ε 780). Trimethylene sulphide showed $\lambda_{max.}$ 270 mμ (ε 380).

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[19] Ohle and Vargha, *Ber.*, 1929, **62**, 2435.