The Preparation of Aldotetroses from Aldopentoses via 1 : 1-*Diethylsulphonyl*-3 : 4 : 5-*trihydroxypent*-1-*enes*.

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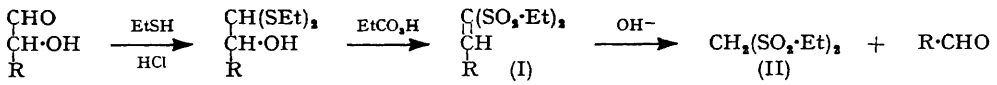
Aldopentose diethyl dithioacetals are oxidised by aqueous peroxypropionic acid to 1 : 1-diethylsulphonyl-3 : 4 : 5-trihydroxypent-1-enes (I; R = trihydroxypropyl) which on treatment with dilute ammonia solution are degraded in high yield to the corresponding aldotetroses. A preliminary account of this work has appeared elsewhere (Hough and Taylor, *Chem. and Ind.*, 1954, 575).

Conventional methods of aldose degradation when applied to the preparation of aldotetroses from aldopentoses are not wholly satisfactory. The yields are generally poor, owing to over-oxidation and epimerisation, and the products are of doubtful purity unless subsequently purified either by chromatography or through crystalline derivatives. Deulofeu (*Adv. Carbohydrate Chem.*, 1949, **4**, 119) and Hockett (*J. Amer. Chem. Soc.*, 1935, **57**, 2260, 2265) have summarised the early work and described some improvements of the Ruff, Wohl, and Zemplén degradations. In the Ruff degradation, which has been improved by use of ion-exchange resins (Diehl, Fletcher, and Hudson, *ibid.*, 1950, **72**, 4546), over-oxidation gives a mixture of triose and tetrose (unpublished observations by J. K. N. Jones and K. B. Taylor) which require separation either by chromatography on cellulose or by fractional distillation of volatile derivatives (Overend, Stacey, and Wiggins, *J.*, 1949, 1358). Hexose oximes have been degraded to pentoses in good yield by 1-fluoro-2 : 4-dinitrobenzene (Weygand and Löwenfeld, *Ber.*, 1950, **83**, 559), but details have not yet been

published of its application to the preparation of tetroses. 3 : 4-Dihydro-3 : 4-dihydroxypyrans (pentals) can be ozonised in acetic acid to tetroses, but the method is tedious and the overall yields low (Freudenberg, *Ber.*, 1932, **65**, 168; Felton and Freudenberg, *J. Amer. Chem. Soc.*, 1935, **57**, 1637). An excellent method for the degradation of D-mannose has been described by McDonald and Fischer (*Biochim. Biophys. Acta*, 1953, **12**, 203) whereby diethylsulphonyl derivatives of the aldose, obtained by oxidation of its diethyl dithioacetal with peroxypropionic acid, are converted in almost quantitative yield into D-arabinose and diethylsulphonylmethane, by treatment with aqueous ammonia. This method is a simplification of that previously described for the degradation of 3 : 4 : 5 : 6-tetra-*O*-acetyl-1 : 1-diethylsulphonylhex-1-enes to pentoses (McDonald and Fischer, *J. Amer. Chem. Soc.*, 1952, **74**, 2087), and D-*arabo*-1 : 3 : 4 : 5 : 6-penta-*O*-acetyl-2 : 2-diethylsulphonylhexane to D-erythrose bisacetamide (Bourne and Stephens, *J.*, 1954, 4009).

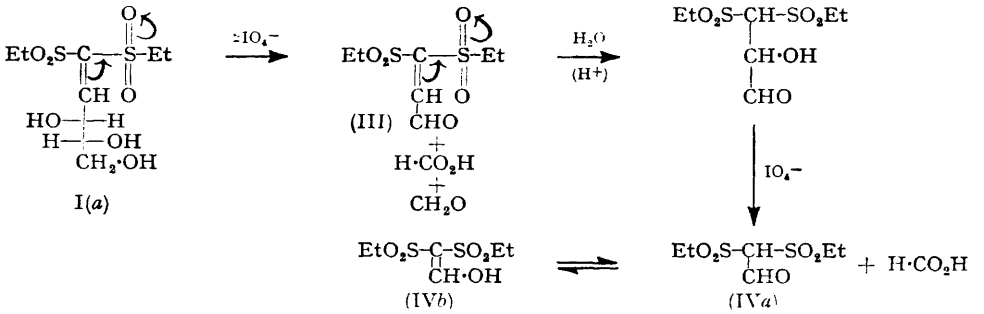
Application of this simplified procedure to the preparation of aldetetroses gave products of high purity in good overall yields (>60%).



Crystalline D-xylose diethyl dithioacetal was prepared directly from D-xylose, ethanethiol, and concentrated hydrochloric acid, purification *via* acetylation and deacetylation being unnecessary (cf. Wolfrom, Newlin, and Stahly, *J. Amer. Chem. Soc.*, 1931, **53**, 4379). Subsequent oxidation with an excess of peroxypropionic acid gave 1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene (I*a*) which on treatment with base underwent scission to D-threose and diethylsulphonylmethane (II). Good yields of tetrose were obtained by use of dilute aqueous ammonia (pH 9—10), but as formation of tetrose proceeded the pH gradually fell to 3—4 and the reaction stopped. Consequently ammonia was added at intervals to ensure completion. Under these conditions a chromatographically pure product was obtained, but when stronger ammonia solution (pH >10) was used, epimerisation and degradation of the tetrose were observed. The hydroxyl form of Amberlite IR-4B resin was also used to cleave the disulphone. A product of high purity, as indicated by paper chromatography, was isolated, but in comparatively poor yield (*ca.* 25%). This may be attributed to a chemical combination of the tetrose or its precursor with the resin, since a further quantity of tetrose (*ca.* 50% of the theoretical amount) could be isolated on treatment of the resin with excess of 0·5N-sulphuric acid. By use of the carbonate form of Amberlite IR-4B resin, similar results were obtained, but yields were lower. However, it has been shown that little or no tetrose is removed on shaking an aqueous solution with the hydroxyl form of Amberlite IR-4B resin, under the conditions used in the degradation. D-Threose formed a highly crystalline benzoylhydrazone which should prove useful for the characterisation of this sugar.

The presence of a double bond in the diethylsulphonylpentene (I*a*) was suggested by its absorption in the ultraviolet region below 215 mμ in 95% ethanol and by mild hydrogenation to form a dihydro-derivative, 1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypentane. Acetylation gave D-*threo*-3 : 4 : 5-tri-*O*-acetyl-1 : 1-diethylsulphonylpent-1-ene, which, like the 3 : 4 : 5 : 6-tetra-*O*-acetyl-1 : 1-diethylsulphonylhex-1-enes, was not degraded when treated with ammonia solution (*d* 0·88) in methanol. Addition at the double bond occurred, forming a 2-amino-1 : 1-diethylsulphonyl derivative, which was isolated as its crystalline tri-*O*-acetyl derivative. The diethylsulphonylpentene (I*a*) neither gave a colour reaction with tetranitromethane nor decolorised bromine in chloroform, but it gave a magenta colour reaction in pyridine solution. The absence of olefinic properties may be attributed to removal of anionoid character from $C_{(1)}$ by the adjacent strongly electrophilic ethylsulphonyl groups. However, $C_{(2)}$ is cationoid and this accounts for the sensitivity of the molecule towards hydroxyl ions and other anionoid groups. A molecular model (Catalin Ltd.) of (I; R = trihydroxypropyl) shows that the double bond is strained. Furthermore, the ethylsulphonyl groups sterically hinder one another, and one of them is also hindered by the hydroxyl group on $C_{(3)}$. Despite this hindrance, $C_{(2)}$ remains clear for hydroxyl-ion attack.

Periodate oxidation of 1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene gave unusual results. Three mols. of periodate were consumed at room temperature and in the dark, with the formation of one mol. of formaldehyde and three equivalents of acid, two of which were formic acid. It has been suggested that the acid which was not volatile in steam was the enolic form (IV*b*) of diethylsulphonylacetaldehyde (IV*a*), formed together



with one mol. of formic acid by oxidation of the αβ-unsaturated aldehyde (III) with one mol. of metaperiodate (Hough and Taylor, *loc. cit.*). Böhme and Wolff (*Ber.*, 1947, **80**, 193) noted that solutions of a related compound, 1 : 1-dimethylsulphonylacetone, showed no carbonyl absorption in the ultraviolet region, and that this compound titrated as a monobasic acid. Attempts to isolate the enol (IV*b*) from the oxidation mixture by chloroform extraction were unsuccessful, only diethylsulphonylmethane being obtained on evaporation of the chloroform. Schröeter (*Annalen*, 1898, **303**, 123) observed that formylmethanedisulphonic acid (V) was decomposed by acid to methanedisulphonic acid

$$\underset{\text{(V)}}{(HO_3S)_2{\cdot}CH{\cdot}CHO} \longrightarrow \underset{\text{(VI)}}{(HO_3S)_2CH_2} + CO$$

(VI) and carbon monoxide. Since formic acid was also taken into the chloroform with (IV), it probably caused decomposition of (IV) into carbon monoxide and diethylsulphonylmethane. Diethylsulphonylmethane rapidly decolourises aqueous iodine in the presence of saturated sodium hydrogen carbonate solution; hence this compound was not present in the original samples taken from the periodate oxidation mixture, as no fading end-points were observed during estimations of periodate uptake by Fleury and Lange's method (*J. Pharm. Chim.*, 1933, **17**, 196; cf. Schwarz, *Chem. and Ind.*, 1954, 1000). Results obtained by the latter method were completely compatible with those obtained by the thiosulphate method (Hughes and Nevell, *Trans. Faraday Soc.*, 1948, **44**, 941). Also this observation indicates that (IV) does not interfere with the Fleury–Lange estimation (cf. Schwarz, *loc. cit.*; Bonner and Drisko, *J. Amer. Chem. Soc.*, 1951, **73**, 3699), probably because it exists in solution as the enol (IV*b*) which has no active hydrogen atom.

Diethylsulphonylmethane was not oxidised by metaperiodate, despite activation of the methylene group by the adjacent ethylsulphonyl groups. This is of interest in view of the suggestions that substituted malondialdehyde systems are oxidised at the active hydrogen atom (cf. Huebner, Ames, and Bubl, *ibid.*, 1946, **68**, 1621; Sprinson and Chargaff, *J. Biol. Chem.*, 1946, **164**, 433), as has been often suggested to account for the over-oxidation of carbohydrates (*e.g.*, Neumüller and Vasseur, *Arkiv Kemi*, 1953, **5**, 235; Head and Hughes, *J.*, 1954, 603). It has been established that an adjacent *free* carboxyl, but not ester group, is necessary for oxidation by periodate of the activated hydrogen to hydroxyl; thus, malonic acid, but not diethyl malonate, is oxidised (Huebner, Ames, and Bubl, *loc. cit.*). However, the evidence for a free aldehyde group is rather inconclusive.

It is also noteworthy that the acetylated 3 : 4 : 5-trihydroxy-1-nitropent-1-enes and 3 : 4 : 5 : 6-tetrahydroxy-1-nitrohex-1-enes, obtained by the action of mild base on the corresponding nitro-alcohols (*e.g.*, Schmidt and Rutz, *Ber.*, 1928, **61**, 2142; Sowden and Fischer, *J. Amer. Chem. Soc.*, 1947, **69**, 1048), bear a structural similarity to the acetylated 1 : 1-diethylsulphonyl-3 : 4 : 5 : 6-tetrahydroxyhex-1-enes (McDonald and Fischer, *loc.*

cit.) and the 1 : 1-diethylsulphonyl-3 : 4 : 5-trihydroxypent-1-enes. However, these unsaturated nitro-compounds are not degraded under mild alkaline conditions and the electrophilic character of the single nitro-group is apparently insufficient to provide the necessary cationoid activity at $C_{(2)}$. A molecular model of this type of compound indicates that the double bond is not strained.

D-Arabinose and D-ribose diethyl dithioacetals were oxidised by an excess of aqueous peroxypropionic acid to 1 : 1-diethylsulphonyl-D-*erythro*-3 : 4 : 5-trihydroxypent-1-ene (I; R = D-*erythro*trihydroxypropyl), which was converted in high yield into D-erythrose and diethylsulphonylmethane. This pentene derivative showed end absorption in the ultraviolet region, was hydrogenated under mild conditions, and gave a magenta colour in pyridine solution.

Experimental

Microanalyses were by Mr. B. S. Noyes of Bristol. Evaporations were under reduced pressure. Paper chromatography was performed by the descending method at room temperature on Whatman No. 1 filter paper with *n*-butanol–pyridine–water (10 : 3 : 3; v/v) as mobile phase and by use of ammoniacal silver nitrate for the detection of the polyhydroxy-compounds. R_f values are approximate. M. p.s of the disulphones were determined on a Kofler microheating stage, since in glass tubes these compounds melted over a wide range, presumably because alkali in the glass degraded them.

D-*Xylose Diethyl Dithioacetal.*—D-Xylose (6 g.) was shaken with ice-cold concentrated hydrochloric acid (6 ml.) and ice-cold ethanethiol (6 g.) until a homogeneous mixture was obtained. After 6 hr., the mixture was diluted with methanol (25 ml.) and neutralised with lead carbonate. The insoluble lead salts were filtered off and washed with boiling methanol (100 ml.). Concentration of the combined filtrate and washings yielded a pale yellow syrup which was twice dissolved in methanol, filtered, and reconcentrated, to leave D-xylose diethyl dithioacetal (8·2 g.; 80%). The sticky crystals were triturated with ether and dried on a porous tile. Recrystallised from methanol–ether, they had m. p. 69—71°, R_f 0·70 (white-centred spot) (Found: C, 42·1; H, 7·5. Calc. for $C_9H_{20}O_4S_2$: C, 42·1; H, 7·8%). (Wolfrom, Newlin, and Stahly, *loc. cit.*, reported m. p. 63—65°.)

Peroxypropionic Acid (d'Ans and Frey, *Ber.*, 1912, **45**, 1845).—Propionic anhydride (30 g.) was mixed with hydrogen peroxide (90—100 vol.; 30 ml.), and to the mixture was added one drop of concentrated sulphuric acid. Usually a vigorous reaction ensued with the evolution of pungent irritating vapour. The mixture was cooled to room temperature; if another drop of acid caused no further vigorous reaction, concentrated sulphuric acid (15 ml.) was carefully added, and then hydrogen peroxide (90—100 vol.; 30 ml.). After 12 hr. at room temperature, the mixture was distilled at 25—30°/15 mm. The aqueous distillate contained sufficient peroxypropionic acid for the oxidation of 10—15 g. of pentose diethyl dithioacetal.

Peroxypropionic acid was extremely painful to the skin.

1 : 1-*Diethylsulphonyl*-D-threo-3 : 4 : 5-*trihydroxypent*-1-*ene.*—To a solution of D-xylose diethyl dithioacetal (7·1 g.) in dioxan (20 ml.) was added, dropwise with shaking, excess of aqueous peroxypropionic acid (150% of theory for 4 mols., based on propionic anhydride). After 10 min. at room temperature, the mixture was cooled in ice for 1 hr. Subsequent concentration yielded a syrup which partially crystallised. To remove traces of peroxypropionic acid, this was twice dissolved in methanol and reconcentrated. It was then crystallised twice from methanol, giving needles of 1 : 1-*diethylsulphonyl*-D-threo-3 : 4 : 5-*trihydroxypent*-1-*ene* (7·9 g.; 94%), m. p. 109—111°, $[\alpha]_D$ +23·8° (*c*, 2·26 in MeOH), R_f 0·72 (Found: C, 35·9; H, 5·8. $C_9H_{18}O_7S_2$ requires C, 35·8; H, 5·9%). Some preparations failed to crystallise, but the syrups were satisfactorily degraded to D-threose in good yield.

D-*Threose.*—(i) 1 : 1-Diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene (4·7 g.) was dissolved in dilute aqueous ammonia (50 ml.; pH 9—10); immediately the solution assumed a yellow colour which rapidly darkened to orange-red. The pH gradually fell to 3—4 and at intervals (initially ½ hr.) had to be restored with more ammonia solution. Paper chromatography indicated that degradation was complete in 48 hr. Diethylsulphonylmethane was removed by filtration and the solution de-ionised with Amberlite IR-120 and IR-4B resins (see Bayly, Bourne, and Stacey, *Nature*, 1951, **168**, 510; 1952, **169**, 876). The neutral solution was then extracted continually with chloroform to remove any remaining diethylsulphonylmethane. Concentration of the aqueous layer yielded a pale yellow syrup of D-threose (1·7 g.; 91%; 68% based on D-xylose), $[\alpha]_D$ −11° (*c*, 2·50 in H_2O). Hockett (*loc. cit.*) quoted $[\alpha]_D$

$-12{\cdot}3°$ (cf. Hockett, Deulofeu, and Mendive, *J. Amer. Chem. Soc.*, 1938, **60**, 278). The product gave one spot (R_f 0·40) only on the paper chromatogram; erythrose (R_f 0·32) and *glycero*-tetrulose (R_f 0·36), which are distinguishable from threose, could not be detected.

(ii) 1 : 1-Diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene (1 g.) in water (10 ml.) was shaken at room temperature with Amberlite IR-4B (hydroxyl form) resin (2 g.) until paper chromatography of the aqueous phase indicated that degradation was complete (*ca.* 2 days). After filtration, the resin was washed by shaking it with water (2 × 50 ml.) for 1—2 hr., then the neutral solution and washings were extracted continuously with chloroform to remove diethylsulphonylmethane. Concentration yielded a colourless syrup of D-threose (0·10 g.; 26%). Further washings with water did not contain threose. Then the resin was shaken with 0·5N-sulphuric acid (100 ml.) for 18 hr., followed by water (50 ml.) for 1—2 hr. After neutralisation ($BaCO_3$), the combined washings were extracted continuously with chloroform to remove any diethylsulphonylmethane. Subsequent concentration yielded a pale yellow syrup of D-threose (0·19 g.; 49%). Both samples of D-threose gave only one spot (R_f 0·40) on the paper chromatogram, but the material obtained from acid washing of the resin showed some impurity which remained on the starting line. The tetroses gave yellow spots with *p*-anisidine hydrochloride spray.

D-Threose phenylosazone had m. p. 164—165° (Found: C, 64·4; H, 6·3; N, 18·9. Calc. for $C_{16}H_{18}O_2N_4$: C, 64·4; H, 6·1; N, 18·8%). D-Threose gave a highly crystalline *benzoylhydrazone* when heated with benzoylhydrazine in a minimum of ethanol at 95—100° for 1 hr. and then cooled. Recrystallisation from ethanol gave fine needles, m. p. 167—168° (decomp.) (Found: C, 55·3; H, 5·9 N, 12·0. $C_{11}H_{14}O_4N_2$ requires C, 55·4; H, 5·9; N, 11·8%).

1 : 1-*Diethylsulphonyl*-D-threo-3 : 4 : 5-*trihydroxypentane*.—1 : 1-Diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene (0·57 g.) in 95% ethanol (15 ml.) was hydrogenated at atmospheric pressure and room temperature in the presence of Raney nickel (5 g.). One mol. of hydrogen was consumed in 45 min. After removal of the catalyst, concentration of the solution yielded a syrup (0·49 g.) which was crystallised twice from methanol; the *pentane* (0·47 g., 82%) had m. p. 111—113°, $[\alpha]_D$ +28·6° (*c*, 1·31 in MeOH), R_f 0·63 (Found: C, 35·5; H, 6·4. $C_9H_{20}O_7S_2$ requires C, 35·5; H, 6·6%).

D-threo-3 : 4 : 5-*Tri*-O-*acetyl*-1 : 1-*diethylsulphonylpent*-1-*ene*.—A solution of 1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene (0·24 g.) in acetic anhydride (5 ml.) containing one drop of concentrated sulphuric acid was heated at 95—100° for ½ hr., and then poured into ice-water. An oil separated; this was extracted with chloroform (2 × 50 ml.), and the extract was washed with sodium carbonate solution and water, and dried ($MgSO_4$). Subsequent concentration of the solution gave a pale yellow syrup (0·28 g.; 80%) of the tri-*O*-acetyl derivative, $[\alpha]_D$ $-11{\cdot}6°$ (*c*, 8·05 in $CHCl_3$).

2-*Acetamido*-D-threo-3 : 4 : 5-*tri*-O-*acetyl*-1 : 1-*diethylsulphonylpentane*.—D-*threo*-3 : 4 : 5-Tri-*O*-acetyl-1 : 1-diethylsulphonylpent-1-ene (0·10 g.) was dissolved in a mixture of ammonia solution (2 ml.; *d* 0·88) and methanol (2 ml.) and set aside at room temperature for 18 hr. A paper chromatogram displayed only one spot (R_f 0·65), presumably due to 2-acetamido-1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypentane (cf. Bourne and Stephens, *loc. cit.*). Concentration yielded a pale yellow syrup which was dried by repeated dissolution in ethanol and reconcentration. The syrup was then acetylated as above. Concentration of the chloroform extract gave a pale yellow syrup which crystallised spontaneously. Recrystallised from ethanol, it gave *needles* (0·056 g.; 46%), m. p. 122—123°, $[\alpha]_D$ +12·9° (*c*, 1·35 in $CHCl_3$) (Found: C, 42·0; H, 6·0; N, 3·0. $C_{17}H_{29}O_{11}S_2N$ requires C, 41·8; H, 6·0; N, 2·9%).

D-*Arabinose Diethyl Dithioacetal* (Fischer, *Ber.*, 1894, **27**, 673).—D-Arabinose (5 g.) was shaken with concentrated hydrochloric acid (5 ml.) and ethanethiol (5 g.) until the crude D-arabinose diethyl dithioacetal separated. After 2 hr., the product was filtered off, washed with light petroleum (b. p. 40—60°), and recrystallised from methanol (5·4 g., 64%); it had m. p. 127—128°, R_f 0·78 (white-centred spot).

D-*Ribose Diethyl Dithioacetal*.—Prepared from D-ribose (1 g.) as for D-xylose diethyl dithioacetal. Paper chromatography showed that the syrupy product (1·5 g.) contained impurities with R_f 0·65 and 0·70 in addition to D-ribose diethyl dithioacetal (R_f 0·79; white-centred spot). After several days, the syrup crystallised; recrystallised from methanol–ether it (1·4 g., 80%) had m. p. 80—82°. Kenner, Rodda, and Todd (*J.*, 1949, 1616) record m. p. 82—83°.

1 : 1-*Diethylsulphonyl*-D-erythro-3 : 4 : 5-*trihydroxypent*-1-*ene*.— (i) D-Arabinose diethyl dithioacetal (5·4 g.) was oxidised as for D-xylose diethyl dithioacetal giving a syrup (6·1 g.) which crystallised during 2 weeks. Recrystallisation (methanol) gave needles of 1 : 1-*diethylsulphonyl*-D-erythro-3 : 4 : 5-*trihydroxypent*-1-*ene* (5·9 g., 92%), m. p. 108—110°, $[\alpha]_D$ $-58°$ (*c*, 2·29 in

MeOH), R_f 0·72 (Found: C, 35·9; H, 5·9. $C_9H_{18}O_7S_2$ requires C, 35·8; H, 5·9%). (ii) D-Ribose diethyl dithioacetal (1·4 g.) was oxidised as for D-xylose diethyl dithioacetal. A syrup (1·6 g.) was obtained which slowly crystallised. Paper chromatography indicated traces of erythrose, presumably produced by degradation of the diethylsulphonyl derivative. Crystallisation from methanol gave material (1·5 g., 90%), m. p. 105—107°, $[\alpha]_D$ −64° (*c*, 1·68 in MeOH), R_f 0·72. *X*-Ray powder photographs of the crystals, obtained from the oxidation of D-arabinose and D-ribose diethyl dithioacetals, were identical and a mixture of the two crystalline products had m. p. 107—109°.

D-*Erythrose*.—1 : 1-Diethylsulphonyl-D-*erythro*-3 : 4 : 5-trihydroxypent-1-ene (5·4 g.) was degraded as for 1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene giving a pale yellow syrup of D-erythrose (1·9 g., 89%; 52% based on D-arabinose; 64% based on D-ribose) which gave one spot (R_f 0·32) on the paper chromatogram, indicating the absence of threose and *glycero*tetrulose. It had $[\alpha]_D$ −15·9° ⟶ −23·1° (48 hr.; *c*, 1·89 in H_2O) which is higher than reported for the D-isomer; cf. Overend, Stacey, and Wiggins (*loc. cit.*), −18·5°; Ruff (*Ber.*, 1899, **32**, 3672), −14·8°. It is, however, within the numerical range of values reported for the L-isomer; cf. Felton and Freudenberg (*loc. cit.*), +30·5°; Wohl (*Ber.*, 1899, **32**, 3667), +32·7°; Weerman (*Rec. Trav. chim.*, 1917, **37**, 16), +23·6°; Deulofeu (*J.*, 1932, 2973), +22·1°; Ruff (*Ber.*, 1901, **34**, 1365), +21·5°.

D-Erythrose was converted into its phenylosazone which had m. p. 164—165° (Found: C, 64·4; H, 6·2; N, 18·5. Calc. for $C_{16}H_{20}O_2N_4$: C, 64·4; H, 6·1; N, 18·8%). D-Erythrose did not form a crystalline benzoylhydrazone.

1 : 1-*Diethylsulphonyl*-D-erythro-3 : 4 : 5-*trihydroxypentane*.—1 : 1-Diethylsulphonyl-D-*erythro*-3 : 4 : 5-trihydroxypent-1-ene (0·66 g.) was hydrogenated as for 1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene. A pale yellow syrup of the hydrogenated material (0·68 g.; R_f 0·64) could not be induced to crystallise.

Periodate Oxidation of 1 : 1-*Diethylsulphonyl*-D-threo-3 : 4 : 5-*trihydroxypent*-1-*ene*.—A mixture of *ca.* 0·3M-sodium metaperiodate (4 ml.) and 1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene (53·3 mg.) in water (5 ml.) was made up to 50 ml. and stored in an amber bottle in the dark. A blank, containing none of the disulphone, was worked concurrently. Samples were taken at intervals for determination of periodate and acid. Two methods for measuring the uptake of sodium metaperiodate were used.

(i) *Arsenite method* (Fleury and Lange, *loc. cit.*). Samples (5 ml.) were taken from the oxidation mixture and from the blank. To each was added saturated sodium hydrogen carbonate solution (10 ml.), *ca.* 0·1N-sodium arsenite solution (4 ml.), and 20% potassium iodide solution (4 ml.). After 15 min., excess of arsenite was titrated with 0·01N-iodine, starch being used as indicator. The end points were sharp.

(ii) *Thiosulphate method* (Hughes and Nevell, *loc. cit.*). Samples (5 ml.) were taken from the oxidation mixture and from the blank. To each was added 2N-sulphuric acid (5—10 ml.) and then 20% potassium iodide (4 ml.). The iodine liberated was titrated with 0·01N-sodium thiosulphate, starch being used as indicator.

Total acidity (Halsall, Hirst, and Jones, *J.*, 1947, 1427) was determined by taking samples (5 ml.) from the oxidation mixture and from the blank, adding ethylene glycol (2 ml.) to each, and 5 min. later, titrating with 0·01N-sodium hydroxide, with methyl red (screened with methylene blue) as indicator.

Formic acid produced was determined by steam distillation of samples (10 ml.) treated with ethylene glycol as above, and titration of the distillate (*ca.* 50 ml.) with 0·01N-sodium hydroxide.

Formaldehyde was determined by Bell's method (*J.*, 1948, 992) but with a phosphate buffer of pH 6·98. 1 : 1-Diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene (17·5 mg.) gave 15·6 mg. of the formaldehyde derivative (m. p. 187—188°), equivalent to 0·92 mol. of formaldehyde liberated.

Results are in the Table.

Time, hr.	$NaIO_4$, uptake, mol., arsenite	thiosulphate	Total acid, equiv.	$H{\cdot}CO_2H$, equiv.
3	2·36	2·37	2·23	—
6	2·55	2·62	2·52	—
24	2·95	2·91	2·76	2·03

Attempted Isolation of Diethylsulphonylacetaldehyde (IV*a*).—An aqueous solution (200 ml.) containing 1 : 1-diethylsulphonyl-D-*threo*-3 : 4 : 5-trihydroxypent-1-ene (2·2 g.) and sodium metaperiodate (5 g.) was stored in an amber bottle in the dark for 24 hr. The solution was

extracted with chloroform (6 × 100 ml.), and the combined extracts dried (Na_2SO_4) and concentrated at room temperature to an acidic syrup (0·5 g.) which rapidly crystallised. Recrystallised from methanol, the product had m. p. 100—102°, not depressed on admixture with authentic diethylsulphonylmethane (Found: C, 30·2; H, 5·7. Calc for $C_5H_{12}O_4S_2$: C, 30·0; H, 6·0%).

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