647. *The Structure of Bornesitol.*

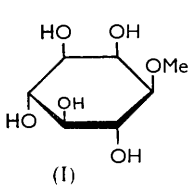
By Shlomo Bien and David Ginsburg.

(−)-Bornesitol isolated from *Lithospermum ruderale* L. has been proved by degradative experiments to possess structure (I).

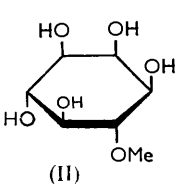
Optically active bornesitol has been isolated from a number of natural sources (see Angyal *et al.* for a recent review [1]). The lævorotatory isomer was isolated in our laboratory in about 1% yield from *Lithospermum ruderale* L.[2] and was shown to be a monomethyl ether of *myo*inositol. Since the compound was optically active it is possible to formulate its structure only as (I) or as (II). Degradative work was undertaken in order to select the correct structure unequivocally.

Notwithstanding the results obtained with our product which " has a similar ionophoretic mobility to (+)-bornesitol but it responded to the detection spray (ammoniacal silver nitrate) slightly differently," [3] and the elegant correlation of dambonitol and racemic bornesitol [1] which appeared while our work was in progress, this communication details the first direct unequivocal proof of the structure of the natural product. The formulation of bornesitol as (I) by previous workers [1,3] has been proved correct.

Demethylation of (−)-bornesitol, $[\alpha]_D^{18}$ −32·05°, was effected by hot concentrated hydriodic acid; *myo*inositol was obtained in 95% yield.



(I)



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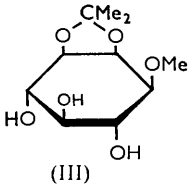

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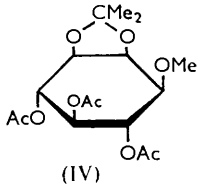


(IV)

(−)-Bornesitol was converted into 1-*O*-methyl-2 : 3-*O*-*iso*propylidene*myo*inositol (III) by treatment with acetone in the presence of acetic acid and zinc chloride under anhydrous conditions. This derivative existed in two dimorphic forms, m. p. 60—62° and 112—114°, respectively, both of which on acetylation in pyridine solution afforded 4 : 5 : 6-tri-*O*-acetyl-1-*O*-methyl-2 : 3-*O*-*iso*propylidene*myo*inositol (IV). The derivative (III) was accompanied by a small quantity of di*iso*propylidene compound which was acetylated under similar conditions.

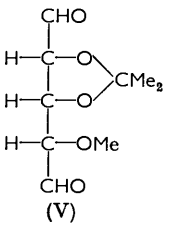
In order to determine whether inversion of configuration occurred during formation of the di*iso*propylidene derivative, it and the mono*iso*propylidene compound were treated separately with boron trifluoride–ether complex in methanol. In each case, (−)-bornesitol was reconstituted in high yield.

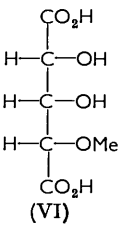
Angyal and Macdonald [4] discussed formation of a tri*iso*propylidene derivative of *epi*inositol and of (−)-inositol in which one *iso*propylidene group must bridge a pair of *trans*-hydroxyl groups, in terms of the conformations of the molecule. It has now been shown that when one equatorial methoxyl group is present in a *myo*inositol derivative, the presence of *one iso*propylidene group bridging a pair of adjacent *cis*-hydroxyl group exerts sufficient influence on the conformation of the molecule to enable a second such group to bridge a pair of adjacent *trans*-hydroxyl groups. However, the positions of the *iso*-propylidene groups in this substance have not been determined.

The mono*iso*propylidene derivative (III) was oxidised with lead tetra-acetate in dry

[1] Angyal, Gilham, and Macdonald, *J.*, 1957, 1417.
[2] Gorman, Bien, and Ginsburg, *Bull. Res. Council Israel*, 1956, **5**, *A*, 253.
[3] Dr. A. B. Foster, personal communication, March 1st, 1956; cf. Foster and Stacey, *Chem. and Ind.*, 1953, 279.
[4] Angyal and Macdonald, *J.*, 1952, 686.

chloroform, affording the syrupy dialdehyde (V). Oxidation of this with bromine-water in the presence of strontium carbonate [5] afforded the strontium salt of the corresponding diacid (VI), which after suitable working up including a demethylation step (see p. 3191) gave a syrup showing the expected infrared absorption for a lactone-acid. Now, if bornesitol possesses structure (I), the lactone-acid should be the γ-lactone of *ribo*trihydroxyglutaric acid,[6] whilst if it possesses structure (II) the γ-lactone of talomucic acid [7] would be expected to be formed at this stage of the degradative procedure. An authentic specimen of the γ-lactone of *ribo*trihydroxyglutaric acid (VII) was prepared from D-(−)-ribose [8] [it does not matter which optical isomer of ribose is used as starting material because the acid (VII) is optically inactive]. The authentic specimen (VII) had m. p. 168—170°. Although the infrared spectra of the authentic sample and of the syrup obtained from the natural product were virtually superimposable [these included bands at 1785 (γ-lactone) and 1735 cm.$^{-1}$ (CO_2H) in KBr], the spectrum of the latter included an additional band at 1630 cm.$^{-1}$, indicating the presence of small quantities of unsaturated impurities. Even seeding of the syrup resulting from the natural product with a small amount of crystalline authentic specimen did not lead to its crystallisation. We therefore turned our attention to an alternative structural proof, namely, to reduction rather than oxidation of the dialdehyde (V).


(V)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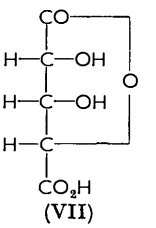
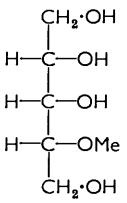
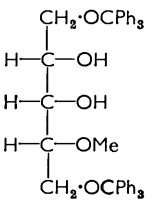

(VII)


(VIII)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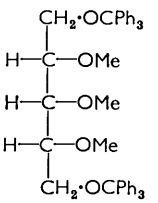
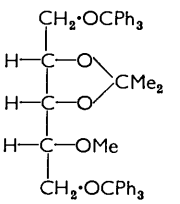

(X)


(XI)

The dialdehyde (V) was reduced with sodium borohydride in methanol solution, and the resulting tetra-alcohol (VIII) was treated with triphenylmethyl chloride in pyridine, affording the ditrityl derivative (IX) accompanied by some monotrityl derivative. The ditrityl compound (IX) was methylated several times with dimethyl sulphate in the presence of sodium hydroxide, giving the trimethyl ditrityl ether (X) and a dimethyl ditrityl ether which could be one of two isomers.

In parallel, ribitol obtained by sodium borohydride reduction of ribose similarly yielded a mixture of the trimethyl ether (X) and a dimethyl ether. Since these two compounds did not depress the melting points of the corresponding ones obtained from natural (−)-bornesitol and since the corresponding infrared spectra were superimposable, it is clear that bornesitol possesses structure (I) and not (II). No effort was expended in working out conditions for complete methylation of the ditrityl compound (IX), since incomplete reaction in both of the above routes afforded two, rather than one, sample for comparison.

[5] Iwadare, *Bull. Chem. Soc. Japan*, 1941, **16**, 40.
[6] Fischer and Piloty, *Ber.*, 1891, **24**, 4222.
[7] Steiger and Reichstein, *Helv. Chim. Acta*, 1936, **19**, 195.
[8] Levene and Jacobs, *Ber.*, 1909, **42**, 3248.

Yet another route was employed to prove the structure of the ether (X). 2 : 3 : 4-Tri-*O*-methylribose [9] was reduced with sodium borohydride and treated with triphenylmethyl chloride, again affording 2 : 3 : 4-tri-*O*-methyl-1 : 5-di-*O*-tritylribitol (X), identical with the substance obtained by degradation of (−)-bornesitol.

The structure of the dimethyl dityityl ether was proved as follows. After treatment with acid the resulting dimethylribitol in aqueous solution was treated with sodium periodate: [10] there was no reaction, as was the case also with the trimethyl dityityl ether. Ribitol and 1 : 5-di-*O*-tritylribitol under these conditions gave, of course, a positive test. The substance in question is therefore formulated as 2 : 4-di-*O*-methyl-1 : 5-di-*O*-tritylribitol.

Di-*O*-tritylribitol has been described previously, and called dityityladonitol,[11] as a compound having m. p. 141—145°. In our hands, during working up of the ribitol tritylation mixture, crystallisation of a mixture of the mono- and the di-trityl derivative afforded a mixture having m. p. 138—146°, but further crystallisation afforded the pure monotrityl derivative, m. p. 141·5° and the pure dityityl derivative, m. p. 156° (see p. 3194). It therefore appears that the previously reported dityityl derivative [11] was, in fact, a mixture. Valentin [11] also reported long melting ranges for other trityl derivatives which he prepared.

By inspection of formula (VIII) and that of the corresponding isomer of the arabitol configuration, it is clear that exhaustive methylation of the former would be expected to give an optically inactive pentamethyl ether whilst the corresponding derivative of the latter should exhibit optical activity. However, since either pentamethyl ether would most likely be a syrup, the above approach using tritylation in order to obtain solid derivatives to effect the structural proof, appeared more reasonable.

Experimental

(−)-*Bornesitol.*—This product crystallised in large transparent rhombs from a boiling methanolic extract of *Lithospermum ruderale* L. after the plant has been defatted with light petroleum; it had m. p. 205—206° (from methanol or aqueous acetone), $[\alpha]_D^{18}$ −32·05° (*c* 3·5 in H_2O) (Found: C, 43·2; H, 7·2; O, 49·7; OMe, 16·5. Calc. for $C_7H_{14}O_6$: C, 43·3; H, 7·3; O, 49·4; OMe, 15·9%).

Demethylation.—(−)-Bornesitol (1 g.) was heated under reflux for 5 min. with 47% hydriodic acid (3 ml.). After cooling, propan-1-ol was added. The product (0·88 g., 95%) had m. p. 225—227° (from aqueous propan-2-ol) and did not depress the m. p. of authentic *myo*inositol. The infrared spectra of the product and its hexa-acetate, m. p. 213° (from methanol), were identical with those of *myo*inositol and its hexa-acetate, respectively.

(−)-*Bornesitol Penta-acetate.*—A solution of (−)-bornesitol (0·1 g.) in pyridine (3 ml.) and acetic anhydride (3 ml.) was warmed on the steam-bath for 5 hr. Evaporation to dryness and crystallisation from methanol afforded the penta-acetate, m. p. 142—143° (0·09 g., 43%). A second m. p., 157°, was observed in some samples of this substance (Found: C, 50·0; H, 6·0; O, 43·55; Ac, 54·1. Calc. for $C_{17}H_{24}O_{11}$: C, 50·5; H, 6·0; O, 43·5; Ac, 53·2%). Plouvier [12] reports m. p. 203—204° for (−)-bornesitol isolated from *Lathrus vernus* Bernh., $[\alpha]_D$ −32°, and double m. p. 142° and 157° for the penta-acetate. The infrared spectrum of our product was identical with that of (±)-bornesitol penta-acetate kindly provided by Dr. L. Anderson.[13]

4 : 5 : 6-*Tri*-O-*acetyl*-1-O-*methyl*-2 : 3-O-iso*propylidene*myo*inositol.*—Dry finely powdered (−)-bornesitol (1·25 g.) and anhydrous zinc chloride (10 g.) were heated with dry acetone (100 ml.) and glacial acetic acid (10 ml.) under reflux for 6—8 hr. The colourless mixture slowly became yellow. Next morning, dry pyridine (45 ml.) was added and the mixture was refrigerated for 4 hr. The precipitated zinc chloride–pyridine complex [14] was removed by

[9] Levene and Tipson, *J. Biol. Chem.*, 1931, **93**, 623.
[10] Feigl, " Spot Tests," 4th edn., Vol. II, p. 102, Elsevier, Amsterdam, 1954.
[11] Valentin, *Coll. Czech. Chem. Comm.*, 1931, **3**, 499 (through *Chem. Abs.*, 1932, **26**, 1577).
[12] Plouvier, *Compt. rend.*, 1955, **241**, 983.
[13] Anderson and Landel, *J. Amer. Chem. Soc.*, 1954, **76**, 6130.
[14] Posternak, *Helv. Chim. Acta*, 1952, **35**, 52.

filtration and washed with a little cold acetone. After concentration of the mother-liquor under reduced pressure to about one-half of its volume the residual complex was again removed. Finally all of the solvents were evaporated under reduced pressure, acetic anhydride (15 ml.) and pyridine (10 ml.) were added, and the mixture was set aside overnight at room temperature. After dilution with chloroform (80 ml.) the solution was washed with ice-cold sodium hydrogen carbonate solution and then with water. The chloroform layer was dried (Na_2SO_4), and the solvents were removed at the water-pump, affording a crude semicrystalline mass (1·9 g.). Crystallisation from ethyl acetate afforded needles of the *monoisopropylidene derivative triacetate*, m. p. 157° (0·85 g.). Two recrystallisations (charcoal) raised the m. p. to 158—159°; $[\alpha]_D^{18}$ was +9·0° (*c* 1·4 in $CHCl_3$) (Found: C, 53·4; H, 6·8; O, 40·25. $C_{16}H_{24}O_9$ requires C, 53·3; H, 6·7; O, 40·0%).

Working up of the mother liquor was difficult as it contained three different acetates. Some success was achieved by evaporation of the mother-liquor to dryness and addition of absolute methanol (12 ml.) and sodium methoxide (0·1 ml. of N-solution) [15] to effect deacetylation of the products. After 24 hr. rhombs of (−)-bornesitol were deposited. The resulting mother liquor was evaporated to dryness and the residue was chromatographed on a cellulose powder column (Whatman standard grade) with acetone–water (4 : 1) as the moving phase and methyl orange to indicate the solvent front. Fractions (5 ml.) were collected. From a residue of 0·36 g. the major portion was collected in the first 8 fractions (0·34 g.). Fractions 1—3 yielded a semi-solid product whilst fractions 4—8 gave a syrup. The former gave, after recrystallisation from a very dilute solution to avoid formation of a gelatinous product, the *diisopropylidene derivative*, m. p. 138—139° (from methyl*cyclo*hexane) (Found: C, 56·05; H, 8·0; O, 35·2; OMe, 11·5. $C_{13}H_{22}O_6$ requires C, 56·9; H, 8·1; O, 35·0; OMe, 11·3%).

The *monoacetate* of the di*iso*propylidene derivative was obtained from this product (40 mg.) by acetic anhydride (3 ml.) in pyridine (3 ml.); it had m. p. 174° (from methyl*cyclo*hexane) (Found: C, 56·3; H, 7·7; OMe, 9·9; Ac, 14·4. $C_{15}H_{24}O_7$ requires C, 56·95; H, 7·65; OMe, 9·8; Ac, 13·6%).

To the di*iso*propylidene derivative (40 mg.) in methanol (1 ml.) boron trifluoride–ether complex (3 drops) was added. Crystals (23 mg.) deposited overnight were (−)-bornesitol (mixed m. p.; penta-acetate).

The syrup in fractions 4—8 (see above) was triturated with ethyl acetate. The *monoisopropylidene derivative* crystallised from this solvent in two dimorphic forms, m. p. 60—62° and m. p. 112—114°, the latter being formed after long storage of a dilute solution (Found: C, 51·5; H, 8·0; O, 40·55. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·75; O, 41·0%). The infrared spectra of both forms (in $CHCl_3$) were identical.

Acetic anhydride in pyridine afforded the triacetate, m. p. 158°, identical with the product described above. Alternatively, deacetylation of the mono*iso*propylidene derivative triacetate with sodium methoxide in methanol afforded either of the dimorphic forms of the mono*iso*propylidene derivative. The crude mono*iso*propylidene derivative usually obtained as a syrup was sufficiently pure for further transformations.

Deacetylation could also be effected by dissolving the compound (0·2 g.) in dry methanol (15 ml.) and saturating the solution (at −10°) with dry ammonia. The solution was kept at 0° for 24 hr. Evaporation gave a syrup from which acetamide was sublimed at 80°/0·01 mm. The resulting syrup (120 mg.) crystallised from ethyl acetate and had m. p. 113°.

Lead Tetra-acetate Oxidation.—To a solution of the crude mono*iso*propylidene derivative (300 mg.) in dry chloroform (5 ml.) was added anhydrous potassium carbonate (0·7 g.) followed, portionwise, by lead tetra-acetate (1·32 g.) with vigorous stirring. The reaction was complete after about 2 hr. (starch–iodide paper). The crystals of lead acetate were removed and washed with chloroform and the combined chloroform solutions were evaporated at 40° at the water-pump. The residue was triturated with dry ether, and additional precipitate was removed. Evaporation and trituration with ether was repeated several times, finally affording a thick syrupy residue of the dialdehyde (V) (240 mg.), $\nu_{max.}$ 1735 cm.$^{-1}$ (saturated C=O).

Reduction of the Dialdehyde.—Small portions of sodium borohydride (120 mg.) were added to a solution of the syrupy dialdehyde (240 mg.) in methanol (5 ml.); the vigorous reaction was moderated by cooling in an ice-bath. After being kept overnight, the mixture was acidified with hydrochloric acid and concentrated, methanol being added repeatedly during the concentration. The product was separated from inorganic salts by several extractions with

[15] Zemplen and Pacsu, *Ber.*, 1929, **62**, 1613.

propan-2-ol. Evaporation of the latter gave a syrup (220 mg.) which showed no C=O absorption in its infrared spectrum (in KBr) and exhibited only a strong band in 3350 $cm.^{-1}$ (OH).

Tritylation and Methylation of Sodium Borohydride Reduction Product.—Triphenylmethyl chloride (0·7 g.) was added to a solution of the above syrupy reduction product (200 mg.) in dry pyridine (2 ml.). The mixture was kept at room temperature for 3 days under anhydrous conditions. The mixture was filtrated from a small amount of precipitate and was diluted with chloroform (30 ml.). The chloroform solution was washed several times with ice-cold sodium hydrogen sulphate solution (5%) and then with water. The chloroform layer was dried (sodium sulphate) and the solvent was removed at the water pump, giving a syrupy residue (730 mg.). The latter was dissolved in benzene (2 ml.) and light petroleum (2 ml.) and was chromatographed on alumina (30 g.; Fisher). Fractions of 25 ml. were taken. Elution with light petroleum gave a semi-solid (*ca.* 60 mg.), m. p. 181° (from propan-2-ol). Infrared absorption showed no free hydroxyl group. This compound is probably 2-*O*-methyl-3 : 4-*O*-*iso*propylidene-1 : 5-di-*O*-tritylribitol (XI) which survived acid hydrolysis after the sodium borohydride reduction.

Elution was continued with benzene, benzene-chloroform and finally with pure chloroform giving oily residues in the various fractions (*ca.* 120 mg.). Infrared absorption (in $CHCl_3$) indicated the presence of trityl groups (strong phenyl absorption at 1600 and 1490 $cm.^{-1}$) and free OH groups (3500 $cm.^{-1}$). Among these fractions [elution with benzene–chloroform (70 : 30)], triphenylmethanol was isolated (350 mg.). All the oily fractions, except those containing triphenylmethanol, were combined and dissolved in acetone (8 ml.). 30% Aqueous sodium hydroxide (5 ml.) and dimethyl sulphate (1·8 ml.) in acetone (3 ml.) were alternately added dropwise with vigorous stirring, so that the solution remained alkaline throughout, the temperature being maintained at 45°. This addition was repeated twice more and a distillation head was attached to the reaction flask; the temperature was slowly raised to 60° and the acetone was removed by distillation. The mixture was stirred at 60° for 2 hr. and at 85° for 1 hr. Dilution with water, extraction with chloroform, and evaporation of the latter gave a syrup which was dissolved in benzene (3 ml.). Slow addition of light petroleum and scratching induced crystallisation. The dimethyl ditrityl ether thus obtained (30 mg.) had m. p. 162—165°. Two recrystallisations raised the m. p. to 183° (from methyl*cyclo*hexane). Admixture with an authentic specimen (see below) caused no depression in m. p. The corresponding infrared spectra were superimposable.

The evaporated mother-liquor was chromatographed in light petroleum–benzene on alumina (Fisher; 10 g.), yielding upon elution with light petroleum–benzene (b. p. 40—60°) the trimethyl ditrityl ether (5 mg.) which was also identical in m. p., mixed m. p. and infrared spectrum with the corrresponding authentic specimen obtained by two alternative routes (see below).

Proof of Structure of Dimethyl Ditrityl Ether.—The following test was worked out. The compound (3 mg.) was dissolved in dioxan (5 drops) and concentrated nitric acid (*d* 1·42; 2 drops) was added. The mixture was kept at room temperature for 10 min. It was diluted with water (2 ml.), the precipitate of triphenylmethanol (when trityl derivatives were tested) was removed by filtration, and the filtrate was treated with sodium periodate solution [10] (1 drop). The dimethyl ditrityl ether gave a negative test and is therefore formulated as 2 : 4-di-*O*-methyl-1 : 5-di-*O*-tritylribitol.

Ribitol and 1 : 5-di-*O*-tritylribitol gave positive tests under these conditions. The trimethyl ditrityl ether (X) gave a negative test.

Ribitol by Reduction of Ribose with Sodium Borohydride.—Sodium borohydride (0·1 g.) in water (5 ml.) was added to a solution of D(−)-ribose (0·5 g.) in water (10 ml.). After being kept overnight at room temperature, the solution was acidified with acetic acid and evaporated to dryness. The residue was heated at 50—60° for 1 hr. with glacial acetic acid (5 ml.), acetic anhydride (5 ml.), and perchloric acid (0·2 ml.), then poured into ice-water and extracted with chloroform. The extract was dried (Na_2SO_4), and the solvent was removed at the water-pump, leaving a syrup (0·8 g.). The syrup was deacetylated by sodium methoxide (0·1 ml. of N-solution) in absolute methanol (12 ml.) at room temperature. Evaporation of the methanol gave a syrupy residue (0·4 g.) which slowly crystallised; it had m. p. 100—101° (from methanol) (lit.,[16] m. p. 102°).

Alternatively, the reduction mixture was acidified with acetic acid and evaporated to dryness. The residue was taken up in water (100 ml.) and the solution was passed through the

[16] Fischer, *Ber.*, 1893, **26**, 633.

acidic form of Amberlite IR-120 (5 g.). The effluent was then percolated through the hydroxylic form of Amberlite IRA-410 (5 g.). Evaporation gave a syrup which slowly crystallised, having m. p. 100—101°, identical with the product described above.

Tritylation of Ribitol.—Triphenylmethyl chloride (4·24 g.) was added to a solution of ribitol (1·12 g.) in dry pyridine (12 ml.). The mixture was kept at room temperature for 4 days. The precipitate was removed and working up was as described above for the natural product. The syrup obtained was triturated with benzene–methyl*cyclo*hexane, giving crystals (4·0 g.), m. p. 138—146°. These were dissolved in a small volume of chloroform and kept at room temperature for 24 hr. The *monotrityl derivative* deposited (0·6 mg.) had m. p. 134—135°, raised by two recrystallisation to 141·5° (from benzene; some sintering at 139°) (Found: C, 72·4; H, 6·6; O, 20·4. $C_{24}H_{26}O_5$ requires C, 73·1; H, 6·6; O, 20·3%).

The chloroform mother-liquor was evaporated to dryness and the residue was crystallised from a minimal volume of methanol. The *ditrityl derivative* thus obtained had m. p. 154—155° which was raised by further recrystallisation to 156° (from benzene–light petroleum or benzene–methyl*cyclo*hexane) (Found: C, 80·7; H, 6·5; O, 12·6. $C_{43}H_{40}O_5$ requires C, 81·1; H, 6·3; O, 12·6%).

The ditrityl derivative (100 mg.) was kept overnight with acetic anhydride (2 ml.) in pyridine (2·5 ml.) at room temperature, the solution was poured into ice-water, and the *triacetate* was removed by filtration; it had m. p. 161° (from methanol) (Found: C, 76·7; H, 5·9; O, 17·0. $C_{49}H_{46}O_8$ requires C, 77·1; H, 6·1; O, 16·8%).

Methylation of Ditritylribitol.—30% Sodium hydroxide solution (24 ml.) and dimethyl sulphate (9 ml.) in acetone (15 ml.) were alternately added with stirring at 50° to ditritylribitol (3·0 g.) in acetone (100 ml.). This procedure was repeated six times so that, in all, the volumes of the added reagents were 125 ml. of alkali and 63 ml. of dimethyl sulphate in 105 ml. of acetone. The mixture was worked up in the usual way (see above) and the syrup thus obtained (3·0 g.) was again methylated as described, yielding a crystalline precipitate, m. p. 164—166°, on trituration with benzene–methyl*cyclo*hexane (1·0 g.). Three recrystallisations gave the *dimethyl ditrityl ether*, m. p. 184° (from methyl*cyclo*hexane) (Found: C, 81·2; H, 6·9; O, 12·2; OMe, 9·1. $C_{45}H_{44}O_5$ requires C, 81·3; H, 6·7; O, 12·0; OMe, 9·3%). The mother-liquor was evaporated and the residue triturated with methyl*cyclo*hexane–light petroleum, affording a crystalline mixture (0·3 g.), m. p. 114—118°, of the above dimethyl ether, the trimethyl ether, and triphenylmethanol which was not separated into its components.

Separation was effected by dissolving the residue from evaporation of the mother-liquor in light petroleum and chromatography on alumina (50 g.; Fisher). Fractions of 25 ml. were taken. Elution with light petroleum gave methyl triphenylmethyl ether (200 mg.) which crystallised (m. p. 81°; from propan-1-ol–methanol) and then sublimed at 78°/0·03 mm. (Found: C, 87·6; H, 6·6; O, 5·8. Calc. for $C_{20}H_{18}O$: C, 87·6; H, 6·9; O, 5·6%).

Elution with light petroleum–benzene (60 : 40) gave the *trimethyl ditrityl ether* (0·5 g.), m. p. 155·5° (from propan-2-ol–methanol) (Found: C, 80·9; H, 6·9; O, 12·2; OMe, 13·5. $C_{46}H_{46}O_5$ requires C, 81·4; H, 6·8; O, 11·8; OMe, 13·7%). Further elution gave triphenylmethanol and partially methylated material which was not investigated.

Reduction of 2 : 3 : 4-*Tri*-O-*methylribose and Tritylation of the Product.*—2 : 3 : 4-Tri-*O*-methylribose [9] (220 mg.) was reduced in methanol (5 ml.) with sodium borohydride (50 mg.). After the usual working up the *diol* was obtained as a mobile liquid (200 mg.). No carbonyl absorption was exhibited in its infrared spectrum in chloroform.

To 2 : 3 : 4-tri-*O*-methylribitol (200 mg.), dissolved in dry pyridine, was added triphenylmethyl chloride (0·7 g.) and the mixture was kept at room temperature for 4 days. After the usual working up the residue (0·75 g.) was chromatographed on alumina (30 g.; Fisher). Elution with light petroleum–benzene (50 : 50) gave the trimethyl ditrityl ether as an oil which crystallised (m. p. 155—156°; from propan-2-ol–ethanol) and was identical with the product described above.

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