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STUDIES OF POLYSACCHARIDE STRUCTURE

PART II. CHARACTERISTIC FRAGMENTS OF A MODIFIED SMITH-DEGRADATION: SYNTHESIS OF SOME NEW METHYL ETHERS OF TETRITOLS

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ABSTRACT

Syntheses of 1-*O*-methyl-D-erythritol, 1-*O*-methyl-L-threitol, 1,4-di-*O*-methylerythritol, and 1,4-di-*O*-methyl-L-threitol are described. These compounds are obtained by a modified Smith-degradation, which involves methylation prior to acid hydrolysis, and reveals the presence of (1→4)- and (1→4,1→6)-linked hexose residues.

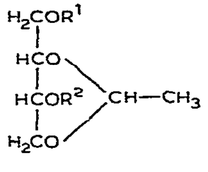
INTRODUCTION

Application of a Smith degradation[1–6], modified by the inclusion of methylation prior to acid hydrolysis, to polysaccharides containing hexose residues linked through positions 4 and 6 yields 1-*O*-methyl-D- or -L-erythritol and 1-*O*-methyl-D- or L-threitol, whereas 1,4-di-*O*-methylerythritol and 1,4-di-*O*-methyl-D- or -L-threitol are obtained from the hexose residues which are linked through position 4. From the viewpoint of structural information, these products are equivalent to the 2,3-di- and 2,3,6-tri-*O*-methylhexoses obtained by conventional methylation analysis. Of the methylated tetritol derivatives, 1-*O*-methyl-D-erythritol and 1,4-di-*O*-methylerythritol were described by Smith *et al.*[7], and we now report on the synthesis of the other members of this group of compounds.

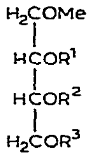
RESULTS AND DISCUSSION

Methylation of 3-*O*-benzyl-2,4-*O*-ethylidene-D-erythritol[8] (**1**) by the Kuhn procedure[9] gave **2** from which 2,4-*O*-ethylidene-1-*O*-methyl-D-erythritol (**3**) was obtained after catalytic hydrogenolysis. Acid hydrolysis of **3** gave syrupy 1-*O*-methyl-D-erythritol (**4**) which was characterized as the known[7] tris(*p*-nitrobenzoate) (**5**). Compound **4** consumed 1.9 mol. of periodate, releasing 0.97 mol. of formic acid. From the oxidation mixture, the known[10] *p*-nitrophenylhydrazone of methoxyacetaldehyde was isolated.

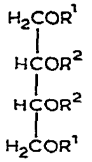
A synthesis of 1,4-di-*O*-methylerythritol was achieved starting from 1,4-di-*O*-tritylerythritol[11] (**6**). Treatment of **6** with benzyl chloride–potassium hydroxide gave the crystalline dibenzyl ether (**7**). The dibenzoate **8** was also crystalline. Both **7** and **8** were detritylated by 90% acetic acid to give the erythritol derivatives **9** and **10**, respectively. Kuhn methylation of **9** gave 2,3-di-*O*-benzyl-1,4-di-*O*-methylerythritol (**11**), and treatment[12] of **10** with diazomethane yielded 2,3-di-*O*-benzoyl-1,4-di-*O*-methylerythritol (**12**). Catalytic debenzylation of **11** over palladium–charcoal and saponification[13] of **10** gave syrupy 1,4-di-*O*-methylerythritol (**13**) which was characterized as the known 2,3-bis(toluene-*p*-sulphonate). Compound **13** consumed 0.97 mol. of periodate without the release of formic acid or formaldehyde.



1 $R^1 = H$, $R^2 = PhCH_2$
2 $R^1 = Me, R^2 = PhCH_2$
3 $R^1 = Me, R^2 = H$

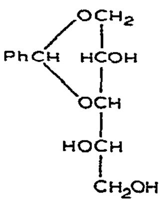


4 $R^1 = R^2 = R^3 = H$
5 $R^1 = R^2 = R^3 = pNO_2Bz$



6 $R^1 = Tr, R^2 = H$
7 $R^1 = Tr, R^2 = PhCH_2$
8 $R^1 = Tr, R^2 = Bz$
9 $R^1 = H$, $R^2 = PhCH_2$
10 $R^1 = H$, $R^2 = Bz$
11 $R^1 = Me, R^2 = PhCH_2$
12 $R^1 = Me, R^2 = Bz$
13 $R^1 = Me, R^2 = H$
14 $R^1 = Me, R^2 = Ts$

1-*O*-Methyl-L-threitol (**22**) was synthesised starting from 1,3-*O*-benzylidene-L-arabinitol[14] (**15**). Treatment of **15** in sequence with periodate and borohydride gave 1,3-*O*-benzylidene-L-threitol[15] (**16**). The crystalline dibenzoate (**17**) of **16** was hydrolysed with 10% acetic acid to give 1,3-di-*O*-benzoyl-L-threitol (**18**). Tritylation of **18** and benzoylation of the product without isolation afforded 1,2,3-tri-*O*-benzoyl-4-*O*-trityl-L-threitol (**19**). Detritylation of **19** with glacial acetic acid gave 2,3,4-tri-*O*-benzoyl-L-threitol (**20**) which was methylated[12] with diazomethane, and the product (**21**) was saponified to give syrupy 1-*O*-methyl-L-threitol (**22**). The structure of **22** was proved by the consumption of 1.89 mol. of periodate, with the concomitant release of 0.95 mol. of formic acid and methoxyacetaldehyde which was characterised as the *p*-nitrophenylhydrazone (71%).



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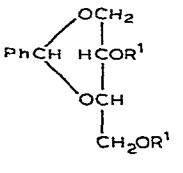
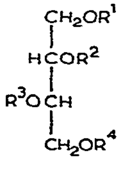
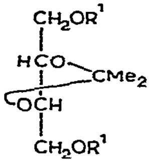


16 $R^1 = H$
17 $R^1 = Bz$

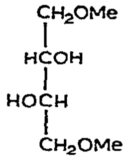


18 $R^1 = R^3 = H, R^2 = R^4 = Bz$
19 $R^1 = Tr$, $R^2 = R^3 = R^4 = Bz$
20 $R^1 = H$, $R^2 = R^3 = R^4 = Bz$
21 $R^1 = Me, R^2 = R^3 = R^4 = Bz$
22 $R^1 = Me. R^2 = R^3 = R^4 = H$

2,3-*O*-Isopropylidene-L-threitol[16] (**23**) was the starting compound for a synthesis of 1,4-di-*O*-methyl-L-threitol (**25**). Kuhn methylation of **23** gave syrupy 2,3-*O*-isopropylidene-1,4-di-*O*-methyl-L-threitol (**24**), hydrolysis of which with 0.4M sulphuric acid gave **25** which was also a syrup.



23 $R^1 = H$
24 $R^1 = Me$



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EXPERIMENTAL

Melting points were determined in a Küstner apparatus and are not corrected. $[\alpha]_D$ values were measured by using a Bellingham–Stanley polarimeter and 1-dm tubes. Purity of compounds was monitored by thin-layer chromatography (t.l.c.) on Kieselgel G (Merck) and detection with 50% sulphuric acid at 130–140°. Consumption of periodate was measured spectrophotometrically[17] and the release of formic acid was determined iodometrically[18,19]

*3-O-Benzyl-2,4-O-ethylidene-1-O-methyl-*D*-erythritol* (**2**). — A solution of 3-*O*-benzyl-2,4-*O*-ethylidene-D-erythritol[8] (7.5 g) in *N*,*N*-dimethylformamide (15 ml) was methylated by the Kuhn procedure, using methyl iodide (22.3 g, 9.9 ml) and silver oxide (9.9 g). The title compound (6.10 g, 76.8%) had b.p. 138–141°/0.3 mmHg, $[\alpha]_D^{22}$ $-42°$ (*c* 0.5, chloroform) (Found: C, 67.01; H, 8.09. $C_{14}H_{20}O_4$ calc.: C, 66.64; H, 7.98%).

*2,4-O-Ethylidene-1-O-methyl-*D*-erythritol* (**3**). — A solution of **2** (4.1 g) in 96% ethanol (45 ml) was hydrogenolysed over palladium–charcoal (0.2 g), and the reaction was followed by t.l.c. After 24 h, no starting material remained and the filtered solution was evaporated to give **3** (2.48 g, 94.3%), $[\alpha]_D^{22}$ $-46°$ (*c* 0.5, ethanol) (Found: C, 51.97; H, 8.81. $C_7H_{14}O_4$ calc.: C, 52.44; H, 8.70%).

*1-O-Methyl-*D*-erythritol* (**4**). — Compound **3** (0.5 g) was hydrolyzed with 0.5M hydrochloric acid in 50% aqueous ethanol (20 ml) at ~95° for 6 h. The solution was neutralized with Amberlite IR-45B (HO^-) resin (5 ml) and then evaporated to give **4** (315 mg, 75%), $[\alpha]_D^{22}$ $-4.8°$ (*c* 1, ethanol); lit.[20] $[\alpha]_D$ $-5°$ (ethanol) (Found: C, 45.08; H, 8.67; OMe, 22.47. $C_5H_{12}O_4$ calc.: C, 44.10; H, 8.88; OMe, 22.35%).

Syrupy **4** (15.21 mg), when oxidized with 15mM sodium metaperiodate (30 ml) at room temperature, consumed 1.96 mol. of oxidant. After acidification of the oxidation mixture, titration with 0.1N sodium thiosulphate indicated the release of 0.97 mol. of formic acid.

A solution of **4** (50 mg) in water (20 ml) was treated with sodium metaperiodate (220 mg) for 24 h. The mixture was then acidified with sulphuric acid (3 ml) and heated to give 3 ml of distillate which was added to a solution of *p*-nitrophenylhydrazine (100 mg) in water (10 ml) and conc. hydrochloric acid (0.1 ml). After 5 min, the precipitate (58 mg, 76%) was collected and crystallized from methanol–water (2:3) to give the *p*-nitrophenylhydrazone of methoxyacetaldehyde, m.p. 115°; lit.[10] 115–115.5°.

Conventional treatment of **4** (13.6 mg) with pyridine (1 ml) and *p*-nitrobenzoyl chloride (110 mg) gave 1-*O*-methyl-2,3,4-tri-*O*-*p*-nitrobenzoyl-D-erythritol (**5**), m.p. 164° (from acetone–ethanol), $[\alpha]_D^{22}$ +82° (*c* 1, chloroform); lit.[20] m.p. 162.5–164°, $[\alpha]_D$ +85° (chloroform).

2,3-Di-O-benzyl-1,4-di-O-tritylerythritol (**7**). — A mixture of 1,4-di-*O*-tritylerythritol (**6**, 18.06 g), benzyl chloride (76.0 g), and powdered potassium hydroxide (33.6 g) was stirred at 105–110° for 6 h. The cooled mixture was treated with water (250 ml) and filtered, and the insoluble material was washed free from benzyl chloride with light petroleum. A solution of the pale-yellow product (19.50 g, 85.1%; m.p. 198–201°) in benzene (200 ml) was decolorised with charcoal (2.0 g). Recrystallisation from the same solvent gave **7** (17.05 g), m.p. 199–201° (Found: C, 84.91; H, 6.53. $C_{54}H_{50}O_4$ calc.: C, 84.89; H, 6.59%).

2,3-Di-O-benzylerythritol (**9**). — A suspension of **7** (2 g) in 96% acetic acid (60 ml) was boiled for 15 min. Water (150 ml) was then added to the cooled mixture and the precipitated triphenylmethanol (1.28 g, 94.1%) was removed. The filtrate was extracted with benzene (3 × 40 ml), and the combined extracts were washed with 5% aqueous sodium hydrogen carbonate and water, and evaporated. The syrupy residue was crystallised from ether–light petroleum to give **9** (0.65 g, 82.2%), m.p. 70–71° (Found: C, 71.89; H, 7.10. $C_{18}H_{22}O_4$ calc.: C, 71.51; H, 7.33%).

2,3-Di-O-benzoyl-1,4-di-O-tritylerythritol (**8**). — To a solution of erythritol (6.16 g) in pyridine (100 ml), trityl chloride (29.27 g) was added. After storage at room temperature for 24 h, pyridine (150 ml) was added, and to the cooled (0°) solution benzoyl chloride (28.1 g) was added in three equal parts at intervals of 30 min. After a further 24 h at room temperature, the mixture was poured into ice–water, and the precipitate was collected, washed with ice–water and 5% aqueous sodium hydrogen carbonate, and then dried over phosphorus pentaoxide. The crude product (36.76 g, 90.1%), when recrystallized thrice from benzene, had m.p. 214–216° (Found: C, 83.44; H, 5.80. $C_{56}H_{46}O_6$ calc.: C, 82.53; H, 5.69%).

2,3-Di-O-benzoylerythritol (**10**). — A suspension of **8** (14.1 g) in 90% acetic acid (250 ml) was boiled for 2 h. Water (500 ml) was then added to the cooled mixture and the precipitated triphenylmethanol was removed. The filtrate was extracted with chloroform (3 × 100 ml), and the combined extracts were washed with 10% aqueous sodium hydrogen carbonate and water, and evaporated. The solid residue was twice recrystallised from ether–light petroleum to give **10** (2.54 g, 45.5%), m.p. 129–131° (Found: C, 65.18; H, 5.39. $C_{18}H_{18}O_6$ calc.: C, 65.44; H, 5.49%).

2,3-Di-O-benzyl-1,4-di-O-methylerythritol (**11**). — A solution of **9** (2.7 g) in *N,N*-dimethylformamide (15 ml) was treated with methyl iodide (12.78 g) followed portionwise with active silver oxide (5.6 g). The product (2.80 g, 94.9%) was an oil

(Found: C, 71.33; H, 7.89; OMe, 18.52. $C_{20}H_{26}O_4$ calc.: C, 72.70; H, 7.93; OMe, 18.78%).

2,3-Di-O-benzoyl-1,4-di-O-methylerythritol (**12**). — A solution of **10** (1.98 g) in dichloromethane (30 ml) was cooled to $-5°$ and treated with boron trifluoride etherate (0.1 ml). A solution of diazomethane (prepared from 10.3 g of *N*-methyl-*N*-nitrosourea) in dichloromethane (100 ml) was then added during 2 h. The mixture was filtered, washed with a small amount of aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated to give **12** (2.01 g, 93.4%), m.p. 149–152° (Found: C, 66.73; H, 6.08; OMe, 17.08. $C_{20}H_{22}O_6$ calc.: C, 67.02; H, 6.19; OMe, 17.32%).

1,4-Di-O-methylerythritol (**13**). — (*a*) A suspension of 10% palladium-on-charcoal (0.2 g) in methanol (100 ml) was saturated with hydrogen and treated with a solution of 2,3-di-*O*-benzyl-1,4-di-*O*-methylerythritol (**11**, 2 g) in methanol (40 ml). Hydrogen uptake (290 ml; calc. 300 ml) was complete in 90 min. The solution was filtered and evaporated to give syrupy **13** (0.84 g, 92.3%) (Found: C, 47.72; H, 9.31; OMe, 41.02. $C_6H_{14}O_4$ calc.: C, 47.97; H, 9.39; OMe, 41.29%). Conventional benzoylation of **13** (50 mg) gave the 2,3-dibenzoate **12** (78 mg, 65%), m.p. 151–152° (from methanol). Conventional toluene-*p*-sulphonylation of **13** gave the 2,3-bis(toluene-*p*-sulphonate) **14**, m.p. 139–140° (from ethanol); lit.[14] m.p. 140°.

(*b*) A solution of 2,3-di-*O*-benzoyl-1,4-di-*O*-methylerythritol (**12**, 1.5 g) in methanol (20 ml) was treated with 0.5M methanolic sodium methoxide (1 ml) at room temperature for 24 h, then neutralised with glacial acetic acid, and evaporated *in vacuo*. To the syrupy residue, water (10 ml) was added and the mixture was steam distilled for 1 h. The residual solution was evaporated and the residue was dried over phosphorus pentaoxide to give **13** (420 mg, 66.8%).

On dissolution of **13** (35.2 mg) in 15mM sodium metaperiodate (30 ml), an uptake of 0.97 mol. of oxidant occurred.

A portion (29 ml) of the final solution was acidified with 0.5M sulphuric acid (2 ml) and heated whilst 4 ml of distillate were collected. To half of the distillate, *p*-nitrophenylhydrazine (50 mg), water (5 ml), and conc. hydrochloric acid (0.1 ml) were added The precipitate collected after 10 min was methoxyacetaldehyde *p*-nitrophenylhydrazone (32 mg), m.p. 115°; lit.[10] m.p. 115–115.5°.

To the other half of the distillate, 2,4-dinitrophenylhydrazine (60 mg), water (5 ml), and conc. hydrochloric acid (0.1 ml) were added. The precipitate collected after 20 min was methoxyacetaldehyde 2,4-dinitrophenylhydrazone (41 mg), m.p. 123–125°; lit.[10] m.p. 124–125°.

1,3-Di-O-benzoyl-2,4-O-benzylidene-L-threitol (**17**). — A solution of 2,4-*O*-benzylidene-L-threitol[14] (1.5 g) in pyridine (12 ml) at $-5°$ was treated dropwise during 30 min with benzoyl chloride (3 g). After 16 h at room temperature, the reaction mixture was processed in the usual manner to give **17** (2.78 g, 93.2%), m.p. 102–103° (from cyclohexane), $[\alpha]_D^{22}$ $+12°$ (*c* 0 4, pyridine) (Found: C, 71.62; H, 5.39. $C_{25}H_{22}O_6$ calc.: C, 71.75; H, 5.30%).

1,3-Di-O-benzoyl-L-threitol (**18**). — A solution of **17** (3.5 g) in ethanol (100 ml) and glacial acetic acid (5 ml) containing a suspension of 10% palladium-on-charcoal

(0.5 g) was shaken with hydrogen. After 6–7 h, t.l.c. showed the absence of starting material (benzene–methanol, 9:1; R_F values: **17** 0.76, **18** 0.28). The filtered solution was evaporated and the residue was dissolved in chloroform (200 ml). The solution was washed with aqueous sodium hydrogen carbonate and water, and evaporated, and the residue was crystallised from ether–light petroleum to give **18** (2.12 g, 76.8%), m.p. 46–52° (Found: C, 65.86; H, 5.29. $C_{18}H_{18}O_6$ calc.: C, 65.44; H, 5.49%).

1,2,3-Tri-O-benzoyl-4-O-trityl-L-threitol (**19**). — A solution of **18** (2 g) and trityl chloride (1.85 g) in pyridine (50 ml) was stored at room temperature for 48 h. To the cooled (0°) mixture, benzoyl chloride (1.27 g) was then added dropwise with stirring during 30 min. After standing at room temperature overnight, the mixture was poured on to ice (150 g). The resulting oil was washed with ice–water, and the crude product (3.25 g, 79.4%) was crystallised from methanol (45 ml) to give **19**, m.p. 178–180°, $[\alpha]_D^{22}$ $-19°$ (*c* 0.5, chloroform) (Found: C, 79.02; H, 5.48. $C_{44}H_{36}O_7$ calc.: C, 78.11; H, 5.36%).

2,3,4-Tri-O-benzoyl-L-threitol (**20**). — Compound **19** (3 g) was boiled with 60% acetic acid (100 ml) for 1 h. The warm solution was diluted with water (50 ml) and refrigerated overnight. The filtered mixture was evaporated, the residue was dissolved in chloroform (50 ml), and the solution was washed with aqueous sodium hydrogen carbonate and water, and then evaporated. The residue (1.86 g, 96.8%) was crystallized from ethanol (12 ml) to give **20**, m.p. 79–82°, $[\alpha]_D^{22}$ $-22°$ (*c* 0.3, chloroform) (Found: C, 70.62; H, 5.26. $C_{25}H_{22}O_7$ calc.: C, 69.11; H, 5.14%).

2,3,4-Tri-O-benzoyl-1-O-methyl-L-threitol (**21**). — A solution of **20** (1.7 g) in dichloromethane (50 ml) at $-5°$ was treated with boron trifluoride etherate (0.05 ml) followed by a solution of diazomethane (prepared from 3 g of *N*-methyl-*N*-nitrosourea) in dichloromethane (50 ml) added dropwise with stirring. After a further hour at $-5°$, the mixture was filtered, washed with aqueous sodium hydrogen carbonate (3 × 20 ml) and water (2 × 20 ml), and then evaporated. The residue (1.52 g, 86.8%) was crystallised from hexane (22 ml) to give **21**, m.p. 68–70°, $[\alpha]_D^{22}$ $-26°$ (*c* 0.2, chloroform) (Found: C, 70.25; H, 5.48; OMe, 7.12. $C_{26}H_{24}O_7$ calc.: C, 69.85; H, 5.39; OMe, 6.92%.

1-O-Methyl-L-threitol (**22**). — Compound **21** (1.3 g) was saponified by treatment overnight with methanol (35 ml) containing 0.5M methanolic sodium methoxide (0.2 ml). The mixture was neutralised with glacial acetic acid and evaporated. A solution of the residue in water (15 ml) was extracted with ether (4 × 20 ml). The aqueous phase was then deionized with Amberlite IR-120(H^+) and IR-45B(HO^-) resins and evaporated to give **22** (265 mg, 67.2%), $[\alpha]_D^{22}$ $-9.6°$ (*c* 0.2, methanol) (Found: C, 44.85; H, 9.06; OMe, 22.48. $C_5H_{12}O_4$ calc.: C, 44.10; H, 8.88; OMe, 22.35%).

2,3-O-Isopropylidene-1,4-di-O-methyl-L-threitol (**24**). — 2,3-*O*-Isopropylidene-L-threitol (6.5 g) was methylated with *N*,*N*-dimethylformamide (50 ml) and methyl iodide (25 ml) in the presence of active silver oxide (25 g) for 48 h. The mixture was treated with chloroform (200 ml), filtered, and evaporated. Distillation of the residue gave **24** (6.75 g, 88.5%), b.p. 102–103°/16–18 mmHg, $[\alpha]_D^{22}$ $-16.5°$ (*c* 0.2, chloroform) (Found: C, 56.19; H, 9.39. $C_9H_{18}O_4$ calc.: C, 56.82; H, 9.53%).

*1,4-Di-O-methyl-*L*-threitol* (**25**). — Compound **24** (5 g) was hydrolysed with 0.5M sulphuric acid (100 ml) at 100° for 6 h. The hydrolysate was neutralised ($BaCO_3$), filtered, and evaporated. Distillation of the residue gave **25** (3.52 g, 89.1%), b.p. 140–150°/0.3–0.4 mmHg, $[\alpha]_D^{22}$ −9.8° (*c* 0.2, ethanol) (Found: C, 47.79; H, 9.47; OMe, 41.67. $C_6H_{14}O_4$ calc.: C, 47.98; H, 9.39; OMe, 41.29%).

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