

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF MINNESOTA]

## Reduction of the Products of Periodate Oxidation of Carbohydrates. VIII. Methylation Studies on D'- and L'-Methoxy-diethylene Glycol and D'-Methoxy-D-hydroxymethyl-diethylene Glycol<sup>1</sup>

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Methyl  $\alpha$ -D-xylopyranoside (I) and methyl  $\alpha$ -D-glucopyranoside (VII) have been oxidized to the corresponding dialdehydes II and VIII with periodic acid. Reduction of the dialdehydes II and VIII with sodium borohydride gave the alcohols III and IX, respectively, which have been completely methylated with sodium and methyl iodide in liquid ammonia to give the corresponding methyl ethers IV and X. Application of the same series of reactions to methyl  $\beta$ -D-xylopyranoside afforded IVa the enantiomorph of IV. Both methylated alcohols IVa and X gave upon hydrolysis methoxyacetaldehyde VI which was identified as the *p*-nitrophenylhydrazone. In addition, the methylated alcohol IVa yielded *O*-methyl ethanol-1,2-diol (V), characterized as its trityl ether, whereas the methylated alcohol X furnished 1,3-di-*O*-methylglycerol (XI), identified as the *p*-nitrobenzoate and as the *p*-toluenesulfonate.

In a previous communication<sup>2</sup> it has been shown that the so-called dialdehydes II and VIII formed by periodate oxidation of methyl  $\alpha$ -D-xylopyranoside (I) and methyl  $\alpha$ -D-glucopyranoside (VII), respectively, can be reduced either catalytically or with sodium borohydride to the corresponding alcohols III and IX. This reduction procedure forms the basis of an alternate method<sup>2,3</sup> to that involving oxidation<sup>4</sup> for the correlation of the structure of methyl glycosides.

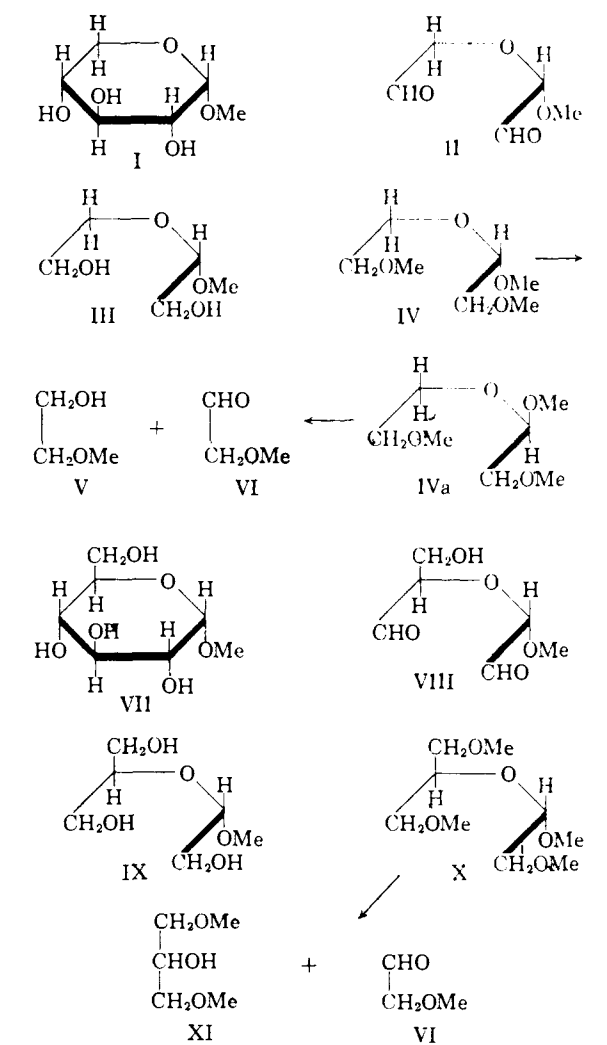
The reaction is not confined to the simple aldehydes for it may be applied to the disaccharides<sup>5</sup> and to the polysaccharides.<sup>5</sup>

The application of periodate oxidation, and then reduction, to polysaccharides<sup>5,6</sup> has provided a new method of end-group assay,<sup>7</sup> the results of which are in good agreement with those from methylation and direct periodate oxidation studies.

Inspection of the formula of these hitherto unknown derivatives of carbohydrate polymers, the polyalcohols, will reveal that methylation studies on them should be capable of throwing considerable light on the structure of the parent polysaccharides.

Before proceeding to methylation studies on the polyalcohols<sup>8</sup> it was decided to examine some simple model compounds in order to establish methylation procedures and to produce certain necessary reference compounds. The two alcohols, D'-methoxy-diethylene glycol (III) and D'-methoxy-D-hydroxymethyl-diethylene glycol (IX), from methyl  $\alpha$ -D-xylopyranoside (I) and methyl  $\alpha$ -D-glucopyranoside (VII), respectively, were selected as the model compounds. The glycosides I and VII were oxidized with periodic acid at room temperature as previously described<sup>2,4</sup> and reduced with sodium borohydride<sup>2</sup> to give the alcohols III and IX, respectively, which were purified by acetylation. The reduction proceeds smoothly and to completion in spite of the fact that the dialdehydes such as II and VIII are known to exist in the cyclic form.<sup>9, 11</sup>

Inspection of the formula of these hitherto unknown derivatives of carbohydrate polymers, the polyalcohols, will reveal that methylation studies on them should be capable of throwing considerable light on the structure of the parent polysaccharides.



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(3) M. Abdel-Akher, J. E. Cadotte, Bertha A. Lewis, R. Montgomery, F. Smith and J. Van Cleve, *Nature*, **171**, 474 (1953).

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(9) J. E. Cadotte, G. G. S. Dutton, I. J. Goldstein, Bertha A. Lewis, F. Smith and J. W. Van Cleve, *THIS JOURNAL*, **79**, 691 (1957).

(10) I. J. Goldstein, Bertha A. Lewis and F. Smith, *ibid.*, **80**, 939 (1958).

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Complete methylation of the alcohols III and IX was not achieved with silver oxide and methyl iodide,<sup>12</sup> but treatment with sodium and methyl iodide in liquid ammonia<sup>13</sup> afforded the fully methylated alcohols IV and X in good yield. The enantiomorph of III obtained from methyl  $\beta$ -D-xylopyranoside readily afforded the enantiomorph of IV, namely, IVa. It is worthy of note that methoxyl determinations carried out on such compounds as IV, IVa, X and the parent alcohols III and IX give high results<sup>2</sup> since additional "alkoxyl" is produced by the ethylene glycol (from III, IV and IVa) and by the glycerol (from IX and X).<sup>8,14</sup> The correct methoxyl content of these compounds can be ascertained, however, by a modified technique<sup>14</sup> which utilizes the fact that methyl iodide forms a crystalline quaternary salt with trimethylamine which is insoluble in propan-2-ol whereas the corresponding salts produced by ethyl and other alkyl iodides are soluble.<sup>15</sup>

Hydrolysis of the methylated dihydric alcohol IVa gave methoxyacetaldehyde (VI), identified as its *p*-nitrophenylhydrazone, and mono-*O*-methylene glycol (*O*-methyl-ethane-1,2-diol) (V), which afforded a crystalline trityl ether.

The methylated trihydric alcohol X yielded upon hydrolysis methoxyacetaldehyde (VI), characterized as described previously, and 1,3-di-*O*-methylglycerol (XI). The latter was characterized as the crystalline *p*-nitrobenzoate and the crystalline *p*-toluenesulfonate.

The observation made herein that such alcohols as III and its enantiomorph, and IX, undergo smooth methylation to give good yields of the corresponding methyl ethers indicates that the same procedure should be applicable to the polyalcohols and thus prove useful in the study of polysaccharides.

### Experimental

Unless stated otherwise all evaporations were carried out *in vacuo* at 40–45° (bath temp.).

**Methyl  $\alpha$ - and  $\beta$ -D-Xylopyranoside.**—The methyl-D-xylopyranosides were prepared as described previously.<sup>16</sup> The methyl  $\beta$ -D-xylopyranoside had m.p. 157°,  $[\alpha]^{20}_D$   $-62.8^\circ$  in water (*c* 3.7), after recrystallization from ethanol, and the methyl  $\alpha$ -D-xylopyranoside, isolated from the mother liquors had m.p. 91°,  $[\alpha]^{20}_D$   $+149^\circ$  in water (*c* 3.2), after recrystallization from ethyl acetate.

**Oxidation of Methyl  $\alpha$ -D-Xylopyranoside with Periodic Acid.**—A solution of methyl  $\alpha$ -D-xylopyranoside (10 g.) in 0.28 *N* periodic acid (1000 ml.) was kept at room temperature for 14 hr. after which time the reaction was complete as indicated by the consumption of 2 molecular proportions of periodate and by the attainment of a constant rotation,  $[\alpha]^{20}_D$   $+119^\circ$  (based on a theoretical yield of the dialdehyde II) a value in good agreement with that ( $+122^\circ$ ) reported previously.<sup>3</sup>

The solution was neutralized with 0.3 *N* barium hydroxide, centrifuged to remove the precipitate, and concentrated to about 600 ml.

**Reduction of D'-Methoxydiglycolic Aldehyde (II) with Sodium Borohydride.**—The solution obtained in the previous experiment was treated with sodium borohydride (2.4 g.)<sup>2,17</sup> when the observed rotation changed from  $+1.60^\circ$

(initial value) to  $-0.06^\circ$  (1 dm. tube) in 10 min. After 3 hr. the alkaline solution was neutralized with carbon dioxide (Dry Ice), filtered, and concentrated to a sirup which was purified by extraction with methanol. Distillation of the sirupy product gave D'-methoxy-diethylene glycol as a colorless liquid, 5.53 g., b.p. (bath temp.) 130–140° (0.001 mm.),  $n^{20}_D$  1.4443,  $[\alpha]^{20}_D$   $-6.9^\circ$  in ethanol (*c* 6).

**Purification of the Alcohol III by Acetylation.**—Since the alcohol III obtained in the previous experiment gave a positive test (turneric paper) for borate, the product (2 g.) was acetylated in the usual way with acetic anhydride (10 ml.) and pyridine (10 ml.). Heat was generated during the addition of the anhydride and the reaction mixture was cooled to keep the temperature below 35°. After keeping overnight the reaction mixture was poured with stirring into ice-water (200 ml.) and 1 hr. later the acetate of III was extracted with chloroform. The combined chloroform extracts were washed with sodium bicarbonate solution, and with water, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated to a sirup. Distillation of the latter gave the diacetate of III as a colorless mobile liquid (2.17 g.), b.p. (bath temp.) 105–110° (0.002 mm.),  $n^{20}_D$  1.4286,  $[\alpha]^{20}_D$   $\pm 0^\circ$  (for the pure liquid).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{16}\text{O}_6$ : C, 49.1; H, 7.3. Found: C, 49.0; H, 7.7.

The diacetate of III (1.85 g.) was dissolved in dry methanol (50 ml.) and sodium (10 mg. approx.) was added to effect deacetylation.<sup>18</sup> The solution was kept at room temperature for 10 hr. and then refluxed for 10 min. The solvent was evaporated and the residue distilled giving D'-methoxy-diethylene glycol (III) as a colorless liquid (0.77 g.), b.p. (bath temp.) 112–114° (0.002 mm.),  $n^{20}_D$  1.4423,  $[\alpha]^{20}_D$   $-7.6^\circ$  in ethanol (*c* 12).

*Anal.* Calcd. for  $\text{C}_6\text{H}_{12}\text{O}_4$ : C, 41.1; H, 8.8. Found: C, 44.2; H, 9.6.

**Methylation of D'-Methoxy-diethylene Glycol with Methyl Sulfate and Sodium Hydroxide.**—The dihydric alcohol III (3 g.) was methylated with methyl sulfate and 30% sodium hydroxide in the usual manner at 50°. The reaction mixture was cooled and extracted with chloroform and the combined chloroform extracts concentrated to give a sirup (0.5 g.), having  $[\alpha]^{20}_D$   $-1.9^\circ$  in ethanol (*c* 10). The low yield resulted from loss of the fairly volatile material by azeotropic distillation when the reaction was completed by heating the methylation mixture on the boiling water-bath.

**L'-Methoxy-diethylene Glycol.**—Methyl  $\beta$ -D-xylopyranoside was oxidized with periodic acid and the dialdehyde so formed was reduced with sodium borohydride as described above for the  $\alpha$ -D-anomer. The resulting alcohol was transformed into the diacetate of L'-methoxy-diethylene glycol with acetic anhydride and pyridine, yield 23.1 g., b.p. (bath temp.) 105–108°,  $n^{20}_D$  1.4277,  $[\alpha]^{20}_D$   $\pm 0^\circ$  (for the pure liquid). Catalytic deacetylation<sup>18</sup> in methanol with sodium methoxide as already described gave L'-methoxy-diethylene glycol which distilled as a colorless oil (13.6 g.), b.p. (bath temp.) 112–117° (0.002 mm.),  $n^{20}_D$  1.4441,  $[\alpha]^{20}_D$   $+6.5^\circ$  in ethanol (*c* 7). The yield was 84% based on the weight of the original methyl  $\beta$ -D-xylopyranoside.

**Methylation of L'-Methoxy-diethylene Glycol.**—The alcohol (12 g.) was dissolved in liquid ammonia (600 ml.) contained in a Dewar flask. Sodium (4.3 g.) was added in small portions to the liquid ammonia solution with gentle stirring. After 1 hr., when a faint blue color still persisted, methyl iodide (16 ml.) was added slowly during 0.5 hr. When the reaction mixture had become clear (after 0.5 hr.) the treatment with sodium and methyl iodide was repeated as before. Liquid ammonia was added from time to time to replace that lost by evaporation. Three methylations were applied in this manner. The Dewar flask was opened and the ammonia allowed to evaporate. Water (50 ml.) was added to the residue and the methylated alcohol was extracted with chloroform. The combined chloroform extracts were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and concentrated *in vacuo* at 20–25° (bath temp.) to a sirup. Distillation of this sirup gave di-*O*-methyl-L'-methoxy-diethylene glycol (IVa) as a colorless liquid (8.4 g., or 63%), b.p. (bath temp.) 65–70° (1 mm.),  $n^{20}_D$  1.4130,  $[\alpha]^{20}_D$   $+3.53^\circ$  (pure liquid),  $[\alpha]^{20}_D$   $+0.33^\circ$  in methanol (*c* 15).

*Anal.* Calcd. for  $\text{C}_7\text{H}_{16}\text{O}_4$ : C, 51.2; H, 9.8; OCII<sub>3</sub>, 56.7. Found: C, 51.2; H, 9.9; OCII<sub>3</sub>,<sup>14</sup> 56.1.

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 (17) M. Abdel Akher, J. K. Hamilton and F. Smith, *ibid.*, **73**, 4691 (1951).

**Hydrolysis of Di-O-methyl-L'-methoxy-diethylene Glycol (IVa).** (a) **Identification of Methoxyacetaldehyde.**—A solution of the methylated alcohol IVa (2 g.) in *N* sulfuric acid (2 ml.) was heated for 15 min. at about 80°. After adding water (5 ml.) the solution was boiled (free flame) and 1.5 ml. of distillate was collected. This distillate (1.5 ml.) containing the methoxyacetaldehyde-water azeotrope was treated with a filtered solution of *p*-nitrophenylhydrazine (0.4 g.) dissolved in a mixture of water (25 ml.) and concentrated hydrochloric acid (0.4 ml.). The dense yellow precipitate which began to separate almost at once was filtered off after 5 min. A longer time should be avoided otherwise the bis-*p*-nitrophenylhydrazone of glyoxal is produced. Recrystallization from ethanol-water (2:3) gave methoxyacetaldehyde *p*-nitrophenylhydrazone, m.p. and mixed m.p. 116°. <sup>19</sup>

*Anal.* Calcd. for C<sub>9</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub>: C, 51.7; H, 5.3; N, 20.1. Found: C, 52.0; H, 5.3; N, 19.9.

(b) **Identification of O-Methyl-ethane-1,2-diol (O-Methyl-ethylene Glycol).**—The acidic distillation residue from (a) above, after removal of the methoxyacetaldehyde-water azeotrope, was neutralized with solid sodium bicarbonate. Ether (25 ml.) was added and then enough sodium sulfate to saturate the aqueous layer. After shaking the mixture the ethereal layer was separated and the aqueous layer reextracted with ether. The ethereal extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. Distillation of the residual liquid gave mono-*O*-methyl-ethylene glycol as a colorless liquid (0.4 g.), b.p. 105–120°.

To a solution of the mono-*O*-methyl-ethylene glycol (0.1 g.) in dry pyridine (2 ml.), trityl bromide (0.4 g.) was added. After the initial heat of reaction had subsided, the reaction mixture was warmed for 5 min. on the steam-bath, cooled and poured into water. Upon trituration with water the oily product crystallized and, after recrystallization from methanol, the *O*-methyl-*O*-trityl-ethylene glycol had m.p. and mixed m.p. 106°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>2</sub>: C, 83.0; H, 7.0. Found: C, 83.3; H, 7.4.

**Methylation of D'-Methoxy-hydroxymethyl-diethylene Glycol. D'-Methoxy-hydroxymethyl-diethylene Glycol.**—Methyl  $\alpha$ -D-glucopyranoside, prepared by the method of Cadotte, *et al.*,<sup>20</sup> m.p. 167°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +155° in water (*c* 1), 30 g., was oxidized with 0.25 *N* periodic acid (3 l.) at room temperature. The reaction was complete in 2 hr. when the solution showed [ $\alpha$ ]<sub>D</sub><sup>25</sup> +118° (based on a theoretical yield of the dialdehyde), constant for a further 3 hr. The solution was neutralized with 0.3 *N* barium hydroxide, centrifuged, and the clear solution treated with sodium borohydride (10 g.). After 4 hr. a second portion (2 g.) of sodium borohydride was added and the solution was allowed to stand overnight. The excess of the borohydride was destroyed with carbon dioxide (Dry Ice) as described before; the solution was filtered and concentrated to a sirup which was purified by extraction with ethanol.

The sirupy product was acetylated with pyridine and acetic anhydride as for the alcohol III. Distillation of the product gave *D'*-methoxy-hydroxymethyl-diethylene glycol triacetate as a colorless liquid (41 g.), b.p. (bath temp.) 135–140° (0.003 mm.), *n*<sub>D</sub><sup>25</sup> 1.4396, density (24°) 1.17, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -18.5° (pure liquid), [ $\alpha$ ]<sub>D</sub><sup>25</sup> -12.8° in methanol (*c* 7.6).

Catalytic deacetylation of this triacetate as described above afforded *D'*-methoxy-hydroxymethyl-diethylene glycol (IX) as a colorless, viscous liquid, 15.1 g., b.p. (bath temp.) 170° (0.002 mm.), *n*<sub>D</sub><sup>25</sup> 1.4664, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -12.4° in ethanol (*c* 3).

In another experiment *D'*-methoxy-*D*-hydroxymethyl-diglycolic aldehyde was reduced with hydrogen and a Raney nickel catalyst as previously recorded<sup>2</sup> giving *D'*-methoxy-hydroxymethyl-diethylene glycol (IX) as a clear, colorless, viscous liquid, b.p. (bath temp.) 170–180° (0.002 mm.), *n*<sub>D</sub><sup>25</sup> 1.4660, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -12.5° in ethanol (*c* 2.5).

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*Anal.* Calcd. for C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>: C, 43.4; H, 8.4. Found: C, 43.5; H, 8.4.

**Tri-O-methyl-D'-methoxy-hydroxymethyl-diethylene Glycol (X).**—Since preliminary experiments showed that methylation with methyl iodide and silver oxide failed to give a fully methylated product, and that methylation with methyl sulfate and alkali did not give a good yield of IV when applied to the alcohol III, the alcohol IX was methylated with sodium and methyl iodide in liquid ammonia as already described above for the *D'*- and *L'*-methoxy-diethylene glycol.

A solution of the trihydric alcohol IX, 3.33 g., in liquid ammonia (600 ml.) was subjected to five successive treatments with a slight excess of sodium and methyl iodide. The trimethyl ether of *D'*-methoxy-hydroxymethyl-diethylene glycol (X) thus produced was a colorless liquid, 3.3 g. or 78% yield, b.p. (bath temp.) 95° (3 mm.), *n*<sub>D</sub><sup>25</sup> 1.4208, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -22.8° (pure liquid).

*Anal.* Calcd. for C<sub>9</sub>H<sub>20</sub>O<sub>6</sub>: C, 52.0; H, 9.7; OCH<sub>3</sub>, 59.6. Found: C, 52.1; H, 9.7; OCH<sub>3</sub>,<sup>14</sup> 59.4.

**Hydrolysis of Tri-O-methyl-D'-methoxy-hydroxymethyl-diethylene Glycol (X).** (a) **Identification of Methoxyacetaldehyde.**—A solution of the methylated alcohol X (2.0 g.) in *N* sulfuric acid (10 ml.) was boiled gently and 3 to 4 ml. of distillate containing the methoxyacetaldehyde was collected. Treatment of this distillate with *p*-nitrophenylhydrazine as described above yielded methoxyacetaldehyde *p*-nitrophenylhydrazone<sup>19</sup> m.p. and mixed m.p. 116°.

(b) **Identification of 1,3-Di-O-methyl-glycerol.**—The acidic distillation residue obtained in (a) above was saturated with ammonium sulfate and extracted with ether. The combined ethereal extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated to a sirup. Distillation of this sirup at atmospheric pressure gave: fraction 1, a colorless liquid, 0.196 g., b.p. (bath temp.) 170°, *n*<sub>D</sub><sup>25</sup> 1.4120; fraction 2, a colorless liquid, 0.379 g., b.p. (bath temp.) 180–190°, *n*<sub>D</sub><sup>25</sup> 1.4175. The physical constants of fraction 2 agree with those of 1,3-di-*O*-methylglycerol, b.p. 169°, *n*<sub>D</sub><sup>25</sup> 1.417.

In another experiment a solution of the trimethyl ether X of *D'*-methoxy-*D*-hydroxymethyl-diethylene glycol (1.5 g.) in 2% methanolic hydrogen chloride was refluxed for 8 hr. After this time, when the solution had become optically inactive, the acid was neutralized (Ag<sub>2</sub>CO<sub>3</sub>), a little charcoal added, and the solution was filtered. After removing the excess of the solvent by distillation (at atmospheric pressure) the residual 1,3-di-*O*-methylglycerol was distilled giving a colorless liquid (0.49 g.) b.p. 160–164°, *n*<sub>D</sub><sup>25</sup> 1.4187.

To a solution of 1,3-di-*O*-methylglycerol (0.28 g.) in dry pyridine (5 ml.), *p*-nitrobenzoyl chloride (0.425 g., 1.5 molar proportions) was added. The mixture was heated for 70 min. at 85°, cooled, treated for 10 min. with 0.5 ml. of water and poured into a saturated solution of sodium bicarbonate (25 ml.). The product was extracted with chloroform and the combined extracts washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to a sirup. Distillation of the *p*-nitrobenzoate *in vacuo* gave a product which crystallized spontaneously on keeping at 2–4°. Recrystallization from light petroleum yielded 1,3-di-*O*-methyl-glycerol *p*-nitrobenzoate, m.p. 42.5°, lit.<sup>21</sup> m.p. 43°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>O<sub>6</sub>N: C, 53.5; H, 5.6; N, 5.2. Found: C, 53.8; H, 5.8; N, 5.5.

To a solution of 1,3-di-*O*-methyl-glycerol (0.108 g.) in dry pyridine (3 ml.) was added *p*-toluenesulfonyl chloride (0.189 g., 1.1 molar proportions). The solution was kept for 24 hr. at room temperature and then poured into water (10 ml.). Extraction with chloroform in the usual way gave a sirupy product, b.p. (bath temp.) 135–140° (0.1 mm.), which crystallized spontaneously on keeping at 5°. After recrystallization from aqueous ethanol and from ether-light petroleum ether, the 1,3-di-*O*-methyl-2-*O*-tosyl-glycerol had m.p. 60°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>O<sub>6</sub>S: C, 52.5; H, 6.6; S, 11.7. Found: C, 52.8; H, 6.7; S, 12.1.

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