POLYOXYETHYLENEGLYCOL ETHERS. PART II*

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Further to the work described in Part I (1), the three ethers $C_8H_{17}O(CH_2CH_2O)_6H$, $C_{16}H_{33}O(CH_2CH_2O)_6H$, and $C_{16}H_{33}O(CH_2CH_2O)_6C_{16}H_{33}$ have been obtained from the reaction between the mono- or di-potassium salt of the hexaoxyethyleneglycol and the appropriate alkyl chloride.

The first two ethers, with terminal hydroxyl groups, are soluble in water and in the usual organic solvents. Their infrared spectra show the typical absorption of the hydroxyl at 3 μ and the broad aliphatic ether band in the 8–9 μ region. A medium band at 13.9 μ is indicative of the paraffin chain.

The last ether, lacking a hydroxyl group, behaves like a saturated hydrocarbon, being hydrophobic and soluble in organic solvents only. Its infrared spectrum is almost identical with that of the corresponding monoether except in the region of the hydroxyl absorption.

EXPERIMENTAL

n-Octylhexaoxyethyleneglycol Ether

Metallic potassium (5.9 g, 0.15 g-atom) was added in small pieces to hexaoxyethyleneglycol (42.4 g, 0.15 mole) and the mixture was stirred and heated at 130° C. After the potassium metal had reacted completely, 1-chlorooctane (25 g, 0.17 mole, b.p. 180° at 758 mm, reported in literature, 181.5° at 765 mm) (2) was added dropwise, the stirring being continued for a further 3 hours. The mixture was then cooled, diluted with acetone, and the potassium chloride was removed by filtration.

The residue was fractionally distilled under reduced pressure, and the fraction of b.p. 150°–180° at 0.1 mm (50 g) was collected. This, when distilled, gave hexaoxyethyleneglycol (b.p. 156° at 0.02 mm, 33 g) and *n*-octylhexaoxyethyleneglycol ether (b.p. 180° at 0.07 mm, 195° at 0.3 mm, n_D^{25} 1.4499, 12.7 g, 20%). The product remained yellowish even after several distillations and it was best purified by chromatography through a silica gel column. A mixture of ethyl ether and methanol, 4:1, eluted the colorless liquid in quantitative yield. Calculated for $C_{20}H_{42}O_7$: C, 60.91%; H, 10.66%. Found: C, 60.39%; H, 10.68%.

Preparation of Hexaoxyethyleneglycol Mono- and Di-hexadecyl Ethers

The reaction was carried out as above using hexaoxyethylene-glycol (25.4 g, 0.09 mole), metallic potassium (3.5 g, 0.09 g-atom), and 1-chlorohexadexane (25 g, 0.1 mole, m.p. 12°, reported in literature 12°) (3). At the end, acetone was added to the cooled mixture and the potassium chloride removed by filtration. From the filtrate separated white crystals of hexaoxyethyleneglycol dihexadecyl ether which was recrystallized from absolute alcohol to a constant m.p. 50° C (7 g, 19%). Calculated for $C_{44}H_{90}O_7$: C, 72.33; H, 12.33. Found: C, 72.33; H, 12.40.

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The residue (24 g) was chromatographed in three portions through silica gel and there was obtained from elution with ethyl ether – methanol 9:1 mixture hexadecylhexaoxyethyleneglycol ether (18.9 g, 43%), which after recrystallization from *n*-hexane had m.p. 37° C. Calculated for $C_{28}H_{58}O_7$: C, 66.40; H, 11.46. Found: C, 66.66; H, 11.58.

1. Gingras, B. A. and Bayley, C. H. Can. J. Chem. **35**, 599 (1957).
2. Vogel, A. I. J. Chem. Soc. 640 (1943).
3. Phillips, J. W. C. and Mumford, S. A. J. Chem. Soc. 1732 (1931).

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SEPARATION OF CARBOHYDRATES ON COCOANUT CHARCOAL COLUMNS

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Chromatographic separation on columns of charcoal–Celite has been widely used for resolving mixtures of oligosaccharides (1, 2, 3, 4, 5, 6) and methylated monosaccharides (7, 8, 9). Although Celite alone has been used for separating sugars (10), its addition to the charcoal has usually only served the purpose of increasing the rate of flow of the eluate through the columns. The commonly used mixture has been that originally suggested by Whistler and Durso (1), consisting of equal parts of Darco G-60 and Celite 535 (4, 6, 9), although "activated charcoal" (3, 11) and "animal charcoal" (8) have also been employed. Recently Jermyn (6) has advocated the use of cellulose powder instead of Celite in order to obtain faster flow. Andrews, Hough, and Powell (12) have suggested the use of very short columns, supported on a sintered plate in a Büchner funnel. This technique obviates the need for the addition of Celite, which is stated to have a tendency to contaminate the fractions obtained.

In the course of an investigation on the constitution of a polysaccharide from milkweed floss (13) it was noticed that cocoanut charcoal (a product of Fisher Scientific Co., Fair Lawn, N.J.), 50–200 mesh, pretreated with 6 *N* hydrochloric acid, water, anhydrous ethanol, and again water, was an excellent material for separating both uronic acids and methylated monosaccharides. The rate of flow, even through long columns, was very rapid. The fractions obtained were very pure and the separations were sharp. When a mixture of uronic acids, obtained on partial hydrolysis of milkweed floss (13), was added to the top of a cocoanut charcoal column (4×12 cm) and eluted with 4, 7, and 15% aqueous ethanol, respectively, three main fractions were obtained, namely a chromatographically pure aldotriouronic acid (0.20 g), 2-*O*-(4-*O*-methyl-D-glucopyranosyluronic acid)-D-xylopyranose (1.30 g) and 4-*O*-methyl-D-glucuronic acid (0.45 g), the latter in admixture with some aldobiouronic acid. Addition of a mixture of sugars obtained from the methylated, reduced, and hydrolyzed aldobiouronic acid (0.57 g) to a similar column (2×10 cm) and elution with 10 and 15% aqueous ethanol gave pure 3,4-di-*O*-methyl-D-xylose and 2,3,4-tri-*O*-methyl-D-glucose, respectively. When a mixture of galactose, glucose, and 4-*O*-methyl-D-glucose was treated similarly, elution with 1.5% ethanol yielded the neutral sugars, while the 4-*O*-methyl-D-glucose was eluted with 5% ethanol.