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Short Communications

Separation by Gas Chromatography of Alcohol-Ethylene Oxide Adducts

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The reaction of long chain alcohols with ethylene oxide results in a mixture of polyethyleneglycol monoalkyl ethers of different molecular weights.[1] The chain length distribution of the components in the reaction mixture has been the subject of several investigations.[2-7] However, the low volatility of the higher polyethers and the complexity of the reaction mixture have made the use of any direct analytical procedure extremely intricate. Puthoff and Benedict [6] found that only the unreacted fatty alcohol and the mono- and diethyleneglycol ethers could be quantitatively determined by gas chromatography, although higher components were detectable. Recently, Gildenberg and Trowbridge [8] reported that gas chromatography of ethylene oxide adducts was greatly facilitated by conversion of the hydroxyl groups to the corresponding acetate esters.

The transformation of alcohols to their trimethylsilyl ethers seems to be a most useful technique in gas chromatographic separations of polyhydric alcohols,[9-10] and I wish to report that this technique can be successfully applied in the separation of ethylene oxide adducts.

Fig. 1a shows a chromatogram obtained by direct, high temperature gas chromatography of an ethoxylation mixture, derived from the base-catalysed reaction of dodecanol-1 with 6 moles of ethylene oxide. The low volatility of the higher components restricts the range of detectable adducts.

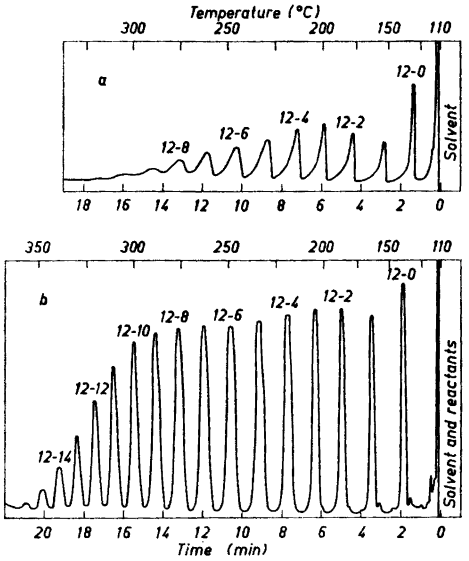

Fig. 1. Separation of polyethyleneglycol monododecyl ethers a) before and b) after silylation.[10] Instrument: Perkin-Elmer 800 Gas Chromatograph with differential flame ionisation detector. Columns: 1/4 inch × 2 feet matched stainless steel columns with 1 % Dow Corning High Vacuum Grease on Chromosorb G 45–60 Mesh. Injector block temperature: 425°C. Column temperature programmed from 110–200°C (15.6°C/min) and from 200–380°C (10.4°C/min). Nitrogen flow 55 ml/min, split ratio 1:4, sample volume 3.0 µl.

For comparison, the excellent separation of the corresponding trimethylsilyl ethers is shown in Fig. 1b. Adducts with as much as 15 ethenoxy units are easily detectable. (In the code used for these chromatograms the first figure represents the carbon number of the fatty alcohol, while the second is the number of ethenoxy units

in the adduct. The identification of the peaks is somewhat tentative.)

Full experimental details of this work will be published later.

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Enhanced Synthesis of Myristic Acid by Rat Liver Homogenates after Addition of Citrate

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The stimulating effect of citrate on lipogenesis was first shown by Brady and Gurin.[1] Later Brady, Mamoon and Stadtman [2] showed that this effect was due partly to citrate generating reduced nicotinamide-adenine-dinucleotide phosphate (NADPH) and Martin and Vagelos [3] and Abraham, Lorch and Chaikoff [4] among others showed that citrate specifically stimulated the acetyl-coenzyme A carboxylase reaction. Many workers have since added citrate to their incubation mediums. Recently Lorch, Abraham and Chaikoff [5] have compared the synthetic patterns of long chain fatty acids formed from ^{14}C-acetate by rat liver slices with the corresponding patterns from synthesis by rat liver homogenates. They show that while synthesis by the slices results in 5 % myristic acid and 53 % palmitic acid, synthesis by citrate stimulated homogenates results in 25 % myristic acid and 33 % palmitic acid when acetate or acetyl-CoA are used as precursors. With malonyl-CoA as the precursor, synthesis by the citrate stimulated homogenates results in nearly the same fatty acid patterns as from the non-stimulated slices (7 % myristic acid and 51 % palmitic acid). These differences are not commented on in relation to the addition of citrate since the experiments include no homogenate incorporations without citrate stimulation. Earlier work by Porter and Tietz [6] with citrate stimulated pigeon liver homogenates and acetate as the precursor resulted in 23 % myristic acid and 64 % palmitic acid. Bhaduri and Srere [7] also base their work on synthesis from acetate by pigeon liver homogenates. They find 24 % myristic acid and 46 % palmitic acid independent of whether they add citrate or not. However, synthesis without citrate is so low that the results seem uncertain.

In our own work we have compared (a) synthesis from ^{14}C-acetate by rat liver slices with synthesis from acetate by nuclei-free reconstructed rat liver homogenates incubated (b) without added citrate as described by Bucher and McGarrahan,[8] (c) with citrate stimulation as described by Catravas and Anker,[9] and (d) with citrate substituted by glucose-6-phosphate and glucose-6-phosphate dehydrogenase in the Catravas and Anker medium. The results from the incorporations by liver slices have been taken from a previous investigation.[10] The total amounts of radioactivity and the relative distributions of these activities among the individual fatty acids were determined by paper chromatography as previously described,[10] except that the assay of the fatty acids from the homogenates in addition also included a more detailed analysis based on extraction and hydrogenation of single fatty acid spots. In a separate experiment we tested the ability of the added glucose-6-