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Silylation and gas-liquid chromatographic analysis of an aqueous polyhydric alcohol mixture

As surveyed elsewhere^{1,2} catalytic high pressure hydrogenolysis of sucrose has been studied in several countries. The process, in general, is carried out in water or a water-alcohol solution. The reaction product is an aqueous polyhydric alcohol mixture and it is impossible to evaporate the water completely. This fact explains why the well-known silylation method of SWEeley *et al.*³, so often applied for the analysis of polyhydric alcohols⁴, has not been used, as far as we know, for the quantitative analysis of the mentioned hydrogenolysis products.

Recently Pierce Chem. Co. announced Tri-sil 'Z' (a mixture of trimethylsilylimidazoles in dry pyridine) as a silylation reagent for hydroxy and polyhydric compounds in either dry or aqueous solution.

This note reports on the use of Tri-sil 'Z' for the quantitative GLC analysis of the reaction product formed during catalytic high pressure hydrogenolysis of sucrose.

It is emphasized that the purpose of this study was not to develop optimum GLC conditions, but to investigate the applicability of the silylation method to our problem.

Materials and methods

*Catalytic hydrogenolysis of sucrose*². A 250 ml autoclave, equipped with a

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vertically pulsating, electromagnetic stirrer, was charged with 50 g sucrose; 5 g catalyst $\text{CuO-CeO}_2\text{-SiO}_2$; 0.5 g Ca(OH)_2 and 75 ml $\text{CH}_3\text{OH-H}_2\text{O}$ (75:25 w/w). Reaction conditions were: 235° ; 200 atm hydrogen pressure; 30 min reaction time. The cooled hydrogenolysis product was filtered off and part of it was distilled to evaporate CH_3OH and H_2O . 10–20 wt. % of water remains in the distilled hydrogenolysis product.

Preparation of the trimethylsilyl derivatives. 1 ml Tri-sil 'Z' was added according to the directions mentioned on the vial to 10–15 mg of the distilled hydrogenolysis product. 25 μl was injected into the gas chromatograph.

Gas chromatography. Apparatus: F & M 810 with a thermal-conductivity cell. Column: 1.5-m stainless steel tube (4 mm I.D.) packed with 20 wt. % Silicone Rubber U.C.W. 98 on 60–80 mesh Diatoport S. Column conditioned with Silyl 8 (Pierce Chem. Co.).

Results and discussion

The following GLC conditions were found to be suitable: carrier gas, hydrogen 60 ml/min; column temperature, $125^\circ\text{--}275^\circ$ with programming at $8^\circ/\text{min}$; injection port, 280° ; detector temperature, 300° . Fig. 1 shows a typical chromatogram.

A number of synthetic polyhydric alcohol mixtures were prepared and dissolved in $\text{CH}_3\text{OH-H}_2\text{O}$. These mixtures were then distilled, silylated and chromatographed in the same way as the hydrogenolysis product. Peak areas were measured with a planimeter and the relative calibration factors calculated.

It was found that: The silylation seems to be complete; the reproducibility of the method is very good; the silylated samples remain unchanged for at least 24 h; the relative errors are $\leq 5\%$. A detailed analysis of the hydrogenolysis product is reported in Table I.

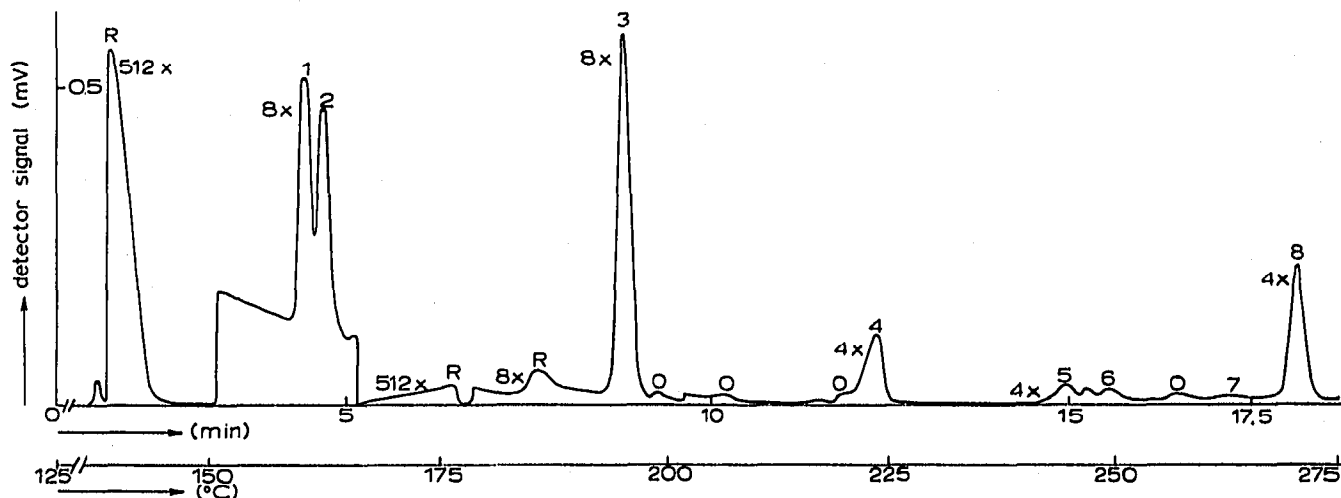


Fig. 1. Gas chromatogram of the silylated reaction product formed during catalytic high pressure hydrogenolysis of sucrose. Column: 1.5-m tube packed with 20 wt. % Silicone Rubber U.C.W. 98 on 60–80 mesh Diatoport S. Carrier gas: hydrogen 60 ml/min. Components: 1 = ethylene glycol; 2 = propane-1,2-diol; 3 = glycerol; 4 = tetrityls; 5 = pentityls; 6 = methylfructofuranosides; 7 = dehydrated hexityls; 8 = hexityls; O = unknown; R = compounds of Tri-sil 'Z'.

TABLE I

DETAILED ANALYSIS OF THE REACTION PRODUCT FORMED DURING CATALYTIC HIGH PRESSURE HYDROGENOLYSIS OF SUCROSE

Components	Weight (%)
ethylene glycol	15.9
propane-1,2-diol	21.1
glycerol	43.0
erytritol	5.4
threitol	1.3
1,2-ethyl-D-fructofuranosides	1.3
dehydrated hexitols	0.2
hexitols	10.1
unknown	1.7
Total	100.0

We concluded that: the silylation method can be applied to the GLC analysis of the hydrogenolysis products described; the accuracy is comparable with other GLC methods¹; one of the advantages of the handsome silylation method compared with acetylation is the saving of time both in sample derivatization and reduction of retention times. With the silylation method it is possible to analyse unreacted saccharides like sucrose, fructose and glucose. This is quite impossible with acetylation.

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