CHROM. 3914

The analysis of oils and fats by gas chromatography

VII. Separation of long-chain fatty alcohols as their trifluoroacetyl and trimethylsilyl derivatives

Long-chain fatty alcohols may be separated by gas chromatography but because of length of analysis time and the tendency for these substances to give tailing peaks it is usual to convert the alcohols to suitable derivatives before gas chromatography. Recently VANDENHEUVEL, GARDNER AND HORNING[1] evaluated ten derivatives for the gas chromatographic analysis of alcohols but only the C_{12}, C_{14}, and C_{16} saturated alcohols were analysed. WOOD[2] has shown that the trifluoroacetyl (TFA) and trimethylsilyl (TMS) derivatives were suitable for the analysis of alcohols. These derivatives have shorter retention times than the corresponding acetyl derivatives. He also indicated that the TFA derivatives of C_{18} unsaturated alcohols gave a better separation than the TMS derivatives on a polar stationary phase but no retention data were given.

ACKMAN[3] has suggested that it is probable that derivatives of unsaturated acids produced by modifying the carboxyl group will have the same Type II separation factors, and JAMIESON AND REID[4] found that long-chain methyl esters, alcohols, acetates and hydrocarbons had the same Type II separation factors on a BDS packed column. The present work investigates the separation of TFA and TMS derivatives of unsaturated alcohols on a polar and two low-polarity stationary phases and compares the separation factors obtained with those given by the corresponding acetyl derivatives.

Experimental

Alcohols were prepared from the corresponding methyl esters by lithium aluminium hydride reduction using the procedure previously described[4]. TFA and TMS derivatives were prepared from the alcohols by the methods described by WOOD and his coworkers[5–7].

Gas chromatography was carried out on a PE 800 gas chromatograph with nitrogen as the carrier gas and the following columns:

(1) EGSS-X open-tubular, 50 m × 0.5 mm stainless steel; 180°; 3 lb./sq. in. N_2;

(2) BDS open-tubular, 50 m × 0.5 mm stainless steel; 190°; 5 lb./sq. in. N_2;

(3) DEGS support-coated open-tubular, 16 m × 0.5 mm stainless steel; 180°; 2 lb./sq. in. N_2.

These columns were purchased from Perkin Elmer Ltd., Beaconsfield.

Results and discussion

Derivatives of C_{18} unsaturated alcohols were separated on the three columns and Type II separation factors calculated from the retention data. These factors are given in Table I. With each of the columns used there is a decrease in the separation factors in the order: acetate, TFA, TMS. Although the 18:1, 18:2, and 18:3 derivatives were separated from each other on all the columns there was a very poor separation of the TMS 18:0,18:1 pair on the low-polarity stationary phases.

TABLE I

TYPE II SEPARATION FACTORS FOR DERIVATIVES OF C_{18} UNSATURATED ALCOHOLS

Type II factor	*Derivative*		
	Acetate	*TFA*	*TMS*
		EGSS-X	
3/6	1.30	1.29	1.27
3/9	1.64	1.59	1.50
6/9	1.26	1.23	1.18
		BDS	
3/6	1.26	1.25	1.22
3/9	1.48	1.48	1.38
6/9	1.19	1.18	1.14
		DEGS (SCOT)	
3/6	1.25	1.19	1.16
3/9	1.48	1.41	1.34
6/9	1.17	1.16	1.14

TABLE II

EQUIVALENT CHAIN LENGTHS OF DERIVATIVES OF UNSATURATED ALCOHOLS SEPARATED ON EGSS-X

Alcohol	*Equivalent chain length*		
	Acetate	*TFA*	*TMS*
18:0	18.00	18.00	18.00
18:1ω9	18.54	18.41	18.38
18:2ω6	19.17	19.06	18.90
18:3ω6	19.68	19.54	19.37
18:3ω3	20.05	19.87	19.63
18:4ω3	20.60	20.34	20.05
20:1ω9	20.48	20.37	20.38
20:2ω9	20.98	20.76	20.60
20:2ω6	21.12	21.00	20.89
20:3ω9	21.36	21.19	21.01
20:3ω6	21.59	21.43	21.26
20:3ω3	21.96	21.74	21.51
20:4ω6	22.08	21.88	21.62
20:4ω3	22.48	22.24	21.94
20:5ω3	23.01	22.66	22.27
22:1ω9	22.36	22.31	22.36
22:5ω3	24.81	24.50	24.15
22:6ω3	25.16	24.86	24.50

The effect of the terminal group on the retention of derivatives of an extended series of unsaturated alcohols on the most polar column (EGSS-X) is shown in Table II. The best separations were achieved using the acetyl derivatives. Some reversals in retention sequence were observed: 18:4ω3 acetate is eluted after 20:1ω9, the corresponding TFA derivatives are almost coincident, and the 18:4ω3 TMS is eluted before the 20:1ω9; 20:5ω3 acetate and TFA are eluted after the corresponding 22:1ω9 derivatives, but the 20:5ω3 TMS is eluted before the 22:1ω9 derivative.

The use of TFA or TMS derivatives for the gas chromatographic separation of long-chain alcohols leads to shorter retention times but there is also a loss in separation compared to the acetyl derivatives.

This work was supported by a grant from the Scientific Research Council (London), which is gratefully acknowledged.

Department of Chemistry, Paisley College of Technology, Paisley (Great Britain)

G. R. JAMIESON
E. H. REID

1 W. J. A. VANDENHEUVEL, W. L. GARDNER AND E. C. HORNING, *J. Chromatog.*, 19 (1965) 263.
2 R. WOOD, *J. Gas Chromatog.*, 6 (1968) 94.
3 R. G. ACKMAN AND R. D. BURGHER, *J. Chromatog.*, 11 (1963) 185.
4 G. R. JAMIESON AND E. H. REID, *J. Chromatog.*, 26 (1967) 8.
5 R. WOOD AND F. SNYDER, *Lipids*, 1 (1966) 62.
6 R. WOOD, E. L. BEVER AND F. SNYDER, *Lipids*, 1 (1966) 399.
7 R. WOOD, P. K. RAJU AND R. REISER, *J. Am. Oil Chemists' Soc.*, 42 (1965) 161.

Received December 12th, 1968

J. Chromatog., 40 (1969) 160–162

CHROM. 3897

Gaschromatographische Trennung von 2-Methyl- und 3-Methylalkanen an gepackten Säulen

Die Trennung von 2- und 3-Methylalkanen an gepackten Säulen ist, trotz vielfacher Bemühungen anderer Arbeitskreise[1–5], wegen ähnlicher Retentionszeiten beider homologen Reihen bis jetzt misslungen. Nach ŠORM[3] und Mitarbeitern wird der Peak eines Gemisches aus 2- und 3-Methylalkanen lediglich in Richtung der Retentionszeit der stärker vertretenen Komponente verschoben. Nur unter extremen Bedingungen gelang es STREIBL UND KONECNY[6] 2- und 3-Methylalkane mit Hilfe der Kapillarchromatographie zu trennen.

Uns glückte erstmalig die Auftrennung von 2- und 3-Methylalkanen an einer gepackten Säule. Als Säulenmaterial diente Chromosorb P mit 5 % Apiezon L. Die beiden homologen Reihen werden—erprobt an 1:1 und 1:2 Mischungen der Standardsubstanzen 2- und 3-Methylpentadecan, -heptadecan, -nonadecan, -heneicosan und -tetracosan—deutlich getrennt. Das Verfahren lässt sich erfolgreich auf natürliche Pflanzenwachse übertragen. Nach unseren Ergebnissen enthält das Blattwachs von *Rosmarinus off.* L. neben verschiedenen Kohlenwasserstoffreihen, über die an anderer Stelle noch berichtet wird, die 2- und 3-Methylalkane im Bereich von C_{16} bis C_{36}. Besonders deutlich verläuft die Trennung im Bereich von C_{16} bis C_{26}. Bei den geradzahligen Isokohlenwasserstoffen des Rosmarinwachses handelt es sich in diesem Bereich um ein Gemisch aus 2- und 3-Methylalkanen, bei denen das 3-Methylalkan dominiert. Die ungeradzahligen Isokohlenwasserstoffe enthalten ebenfalls beide