Journal of Chromatography, 448 (1988) 428–432
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 689

Note

Gas chromatographic analysis of underivatized resin acids

ROLF GREF

Department of Forest Genetics and Plant Physiology, The Swedish University of Agricultural Sciences, S-901 83 Umeå (Sweden)

(First received February 26th, 1988; revised manuscript received May 30th, 1988)

Resin acids are diterpenes of the abietane, pimarane or labdane types. They are characteristic compounds of conifers and often comprise the major portion of the lipophilic extractives.

Gas–liquid chromatography (GLC) is the prevailing technique for the analysis of diterpene resin acids. Usually they are converted into their corresponding methyl esters prior to analysis. Holmbom[1,2], Nestler and Zinkel[3] and Foster and Zinkel[4] have reported retention data for resin acid methyl esters on non-polar and polar packed or wall-coated open-tubular capillary columns. Zinkel *et al.*[5] have reported on the GLC of trimethylsilyl (TMS) esters of resin acids and conclude that such esters are rapidly hydrolyzed on most polar liquid phases.

This paper describes the GLC of underivatized resin acids on a non-polar fused-silica capillary column.

EXPERIMENTAL

Chemicals

The following pure resin acid standards were analysed: abietic, dehydroabietic, isopimaric, levopimaric, manoyloxid and pinifolic acids. A Portugese gum rosin was also analysed.

Heptadecanoic acid (10 mg) was added to each sample as an internal standard. A portion of each standard was converted into the corresponding methyl ester with freshly prepared diazomethane in diethyl ether–methanol (90:10, v/v). Prior to the GC analyses the samples were dissolved in hexane–ethyl acetate (80:20, v/v).

Gas–liquid chromatography

A Varian 3700 gas chromatograph equipped with a split/splitless capillary injector and flame ionization detection (FID) was used. The injector was equipped with a glass precolumn (70 mm × 2 mm I.D.) packed with 1.5% SE-30 on Chromosorb W HP (80–100 mesh). A fused-silica capillary column (15 m × 0.25 mm I.D.) with a 0.25-μm film of DB-1 (J & W Scientific) was used. The hydrogen carrier gas flow-rate was 1.60 ml/min (56 cm/s). Analyses were done with a 20:1 splitting ratio. The chromatograph was operated isothermally at 210 or 230°C. The injector and detector temperatures were kept at 300°C. Peak aras relative to the internal standard and retention times were measured with a Varian CDS 111 integrator.

0021-9673/88/$03.50

RESULTS AND DISCUSSION

Typical gas chromatograms obtained for the gum rosin are shown in Fig. 1 and the relative retention times of the resin acids and their methyl esters are given in Table I. The monocarboxylic resin acids were almost equally well resolved underivatized at 230°C as their corresponding methyl esters at 210°C. Although underivatized pimaric–sandaracopimaric and isopimaric/levopimaric/palustric–dehydroabietic acids did not show baseline separation, the resolutions were acceptable. Also the overall analysis time was short, being completed in 5 min. At 230°C the methylated acids were subject to some overlapping. The non-polar DB-1 column did not resolve

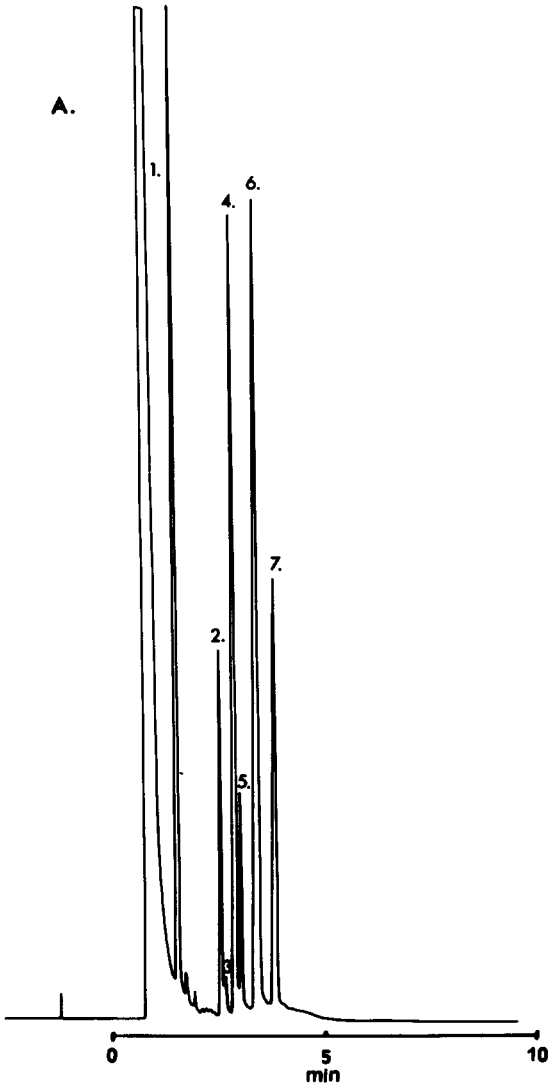

Fig. 1.

(Continued on p. 430)

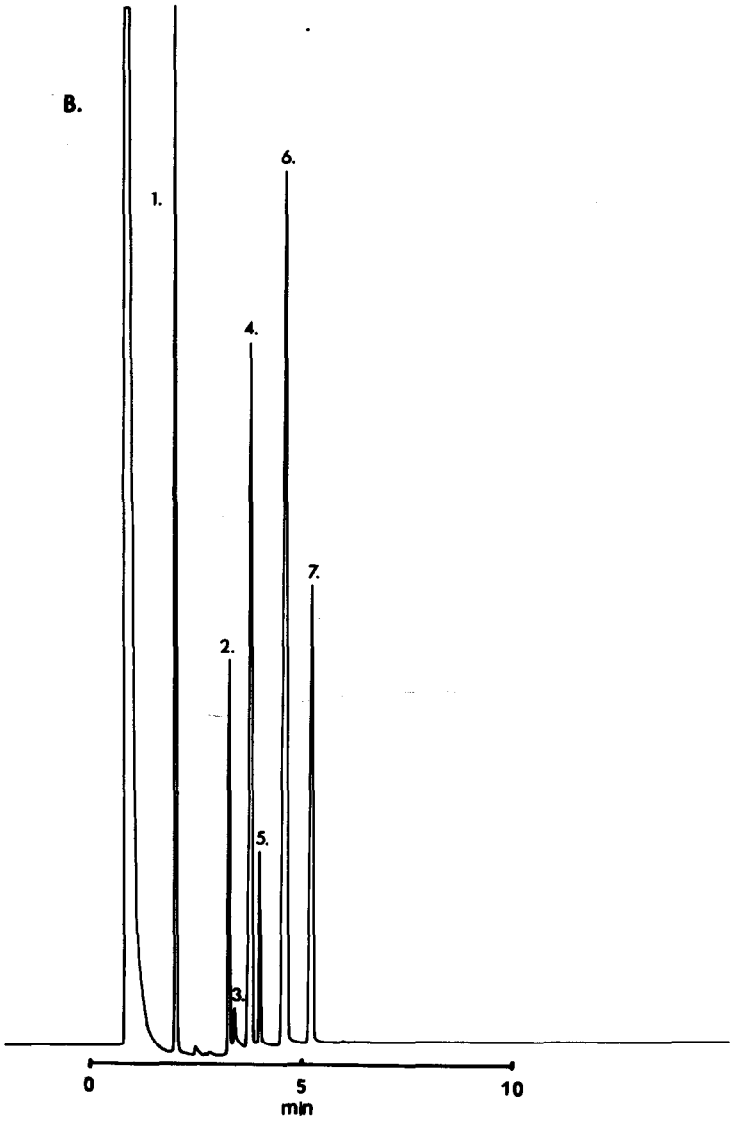

Fig. 1. GC analyses of underivatized resin acids (A) at 230°C and of methylated resin acids (B) at 210°C in Portugese gum rosin. Column: DB-1, 15 m × 0.25 mm I.D. Carrier gas: hydrogen, 1.60 ml/min. Peaks: 1 = heptadecanoic acid (internal standard); 2 = primaric; 3 = sandaracopimaric; 4 = levopimaric + palustric + isopimaric; 5 = dehydroabietic; 6 = abietic; 7 = neoabietic.

isopimaric, levopimaric and palustric acids, underivatized or as their methyl esters. The dicarboxylic pinifolic acid was not eluted unmethylated, even at 300°C.

Tests with the DB-1 column at 230°C gave theoretical plate values for underivatized resin acids of 1700–2100/m and for their corresponding methyl esters at 210°C of 3500–4900/m.

Heptadecanoic acid was shown to be a suitable internal standard for the GC

TABLE I

RELATIVE RETENTION TIMES OF RESIN ACIDS AND THEIR CORRESPONDING METHYL ESTERS ON A DB-1 FUSED-SILICA CAPILLARY COLUMN

Retentions relative to heptadecanoic acid or methyl heptadecanoate

	Relative retention time		
	Resin acid column temp. 230°C	*Resin acid methyl ester column temp.*	
		230°C	*210°C*
Pimaric	1.86	1.64	1.78
Sandaracopimaric	1.92	1.9	1.85
Isopimaric + levopimaric + palastric	2.16	1.86	2.11
Dydroabietic	2.26	1.95	2.23
Abietic	2.63	2.25	2.63
Neoabietic	2.96	2.53	3.01
Manoyloxid	1.88	1.66	1.82
Pinifolic	–	2.83	3.53

analyses of underivatized resin acids because it was completely separated from other compounds of interest in the samples. The quantitative behaviour of the underivatized resin acids and their methyl esters in separate 30-mg samples of Portugese gum rosin is shown in Table II. The values are uncorrected for differences in detector responses. As is seen, the values are in acceptable accordance with each other and some of the divergences must be attributed to poor performance of the split injector in quantitative analyses.

The monobasic resin acids are readily analysed without derivatization by gas chromatography with a non-polar DB-1 fused-silica capillary column using hydrogen as the carrier gas. A column temperature of 230°C seems to be optimal giving acceptable resolution of the most common resin acids (with the exception of isopimaric, levopimaric and palustric acids).

TABLE II

COMPARISON OF QUANTITATIVE BEHAVIOUR OF UNDERIVATIZED AND METHYLATED RESIN ACIDS FROM GUM ROSIN ON A NON-POLAR DB-1 FUSED-SILICA CAPILLARY COLUMN

Values (mean and S.D.) are means from five analyses.

	Composition (%, w/w)	
	Resin acid column temp. 230°C	*Resin acid methyl ester column temp. 210°C*
Pimaric	8.12 (0.08)	8.31 (0.07)
Sandaracopimaric	1.96 (0.02)	1.91 (0.01)
Isopimaric + levopimaric + palustric	24.23 (0.40)	24.99 (0.27)
Dehydroabietic	5.73 (0.10)	4.72 (0.08)
Abietic	39.53 (0.70)	40.58 (0.50)
Neoabietic	20.42 (0.6)	19.50 (0.26)

The use of an appropriate internal standard like heptadecanoic acid gives comparable results for the composition and standard deviation to those obtained by GC of methylated samples of resin acids in, *e.g.*, rosins and oleoresin. A direct method for analysis of underivatized resin acids would be useful for on-line quality control in rosin/tall oil distillation. The major advantage of the method is a decrease in both the preparation and analysis time which minimizes losses and alterations of the samples. The durability of the column has been found not to be affected by injections of underivatized resin acids.

ACKNOWLEDGEMENT

The author is greatful to Professor B. Holmbom for helpful discussions and a gift of the reference sample.

REFERENCES

1 B. Holmbom, *J. Am. Oil Chem. Soc.*, 54 (1977) 289.
2 B. Holmbom, *J. Am. Oil Chem. Soc.*, 55 (1978) 876.
3 F. H. M. Nestler and D. Zinkel, *Anal. Chem.*, 39 (1967) 1118.
4 D. O. Foster and D. F. Zinkel, *J. Chromatogr.*, 248 (1982) 89.
5 D. F. Zinkel, M. B. Lathrop and L. C. Zank, *J. Gas Chromatogr.*, 6 (1968) 158.