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Note

Comparison of relative retention times of volatile oil constituents on capillary columns with those from packed columns

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In 1970, Breckler and Betts[1] reported on the gas chromatographic (GC) relative retention times ($t_{R,rel}$) of various monoterpene and C_{10}-aromatic volatile oil components using packed columns. Changes in $t_{R,rel}$ to linalool were noted for 15°C changes in column temperature over the range 160–220°C. Such high temperatures were necessary as the stationary phase loading was at the high level of 15% for both polar and non-polar columns. The solutes examined in 1970 were divided into five groups: low polarity, A1 (terpenyl acetates) and A2 (terpene hydrocarbons and some terpenoids such as *iso*-menthone) and higher polarity, B1 (terpenols), B2 (aromatic compounds) and B3 (terpene carbonyls, mainly). It was suggested that these groupings could function as an aid to identifying unknown peaks in volatile oil chromatograms. Here, these results are compared with those on capillary columns, which are used at lower temperatures but may not give superior results to the packed columns.

EXPERIMENTAL

Apparatus and materials

A Hewlett-Packard 5790A gas chromatograph was used, fitted with a flame-ionization detector and capillary column control unit. The recorder was a Hewlett-Packard 3380A.

Two Hewlett-Packard fused-silica capillary columns approximately 25 m long 0.21 mm I.D., were used containing: (a) high-performance cross-linked methyl silicone (MeSi) or (b) Carbowax 20M (polyethylene glycol).

Helium was the mobile phase gas, passing through the capillary at about 1 ml min^{-1} (also used as make-up gas for the detector). Retention time of the standard linalool ranged from 0.85 to 1.25 min.

The twelve volatile oil constituents studied were obtained from various commercial sources and donations. Their chromatograms showed only small impurity peaks.

RESULTS AND DISCUSSION

Results from the capillary columns are given in Table I and displayed in Figs.

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TABLE I

RETENTION TIMES RELATIVE TO LINALOOL OF SOME C_{10}-CONSTITUENTS OF VOLATILE OILS ON CAPILLARY COLUMNS

Substances grouped below under A1, A2, B1, B2 and B3 were so assigned by work in 1970 on packed columns[1]. The present results indicate they should remain there, as A group substances show higher $t_{R,rel}$ on the non-polar MeSi capillary and B group substances on the polar Carbowax 20M capillary.

Group	*Substance*	*Capillary temperature*		
		120°C	*135°C*	*150°C*
A1	Citronellyl acetate (CA)			
	MeSi	3.10	2.47	2.04
	20M	1.51	1.34	1.25
	Terpinyl acetate (TA)			
	MeSi	3.08	2.49	2.09
	20M	1.70	1.47	1.35
A2	Iso-menthone (IM)			
	MeSi	1.25	1.21	1.18
	20M	0.88	0.90	1.01
	Limonene (LN)			
	MeSi	0.81	0.88	0.92
	20M	0.56	0.67	0.80
A revised	Pulegone (PU)			
	MeSi	1.81	1.60	1.47
	20M	1.41	1.30	1.26
	Menthol (MN)			
	MeSi	1.38	1.30	1.24
	20M	1.37	1.23	1.18
	Camphor (CP)			
	MeSi	1.20	1.19	1.17
	20M	0.99	1.01	1.07
A/B?	Estagole (ES)			
	MeSi	1.49	1.38	1.28
	20M	1.51	1.36	1.26
B1	Citronellol (CT)			
	20M	2.16	1.70	1.47
	MeSi	1.66	1.49	1.37
B2	Anethole (AN)			
	20M	2.65	2.07	1.74
	MeSi	2.24	1.88	1.65
B3	Carvone (CV)			
	20M	1.88	1.63	1.49
	MeSi	1.80	1.62	1.47

1 and 2, where they are related to the 1970 results on packed columns. Four of the eleven substances need reconsideration on the basis of these new results.

On the non-polar MeSi capillary the two representatives of low-polarity group A1, terpinyl and citronellyl acetates, gave results comparable to those on the packed SE-30 column, although they cannot now be distinguished, in contrast to using the latter (Fig. 1). The low polarity A2 terpene hydrocarbon, limonene also gave comparable results, but the other A2 representative, *iso*-menthone, whilst yielding again an almost unchanging $t_{R,rel}$, gave values lower than those on the packed column,

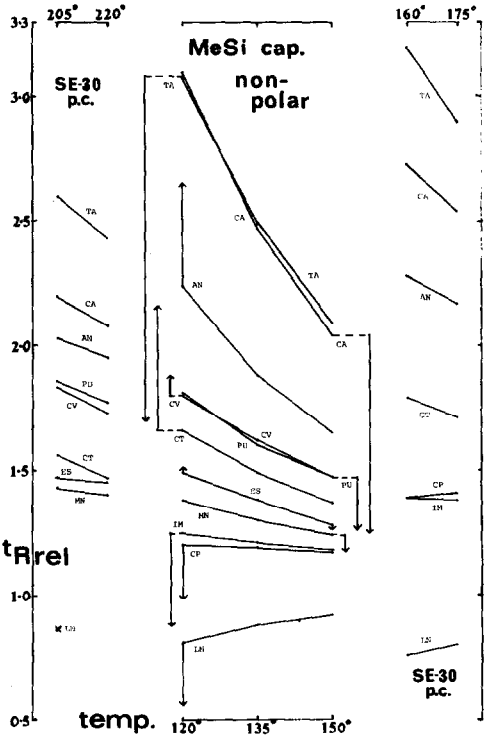

Fig. 1. Relative GC retention times (to linalool) plotted against corresponding temperatures of a non-polar methyl polysiloxane capillary (cap.)/packed column (p.c.). The present capillary results are shown centrally, with 1970 values[1] for the packed column on the left (high temperatures) and right (low temperatures). Abbreviations for substances are given in Table I. Vertical arrows indicate the $t_{R,rel}$ for the same substance on the polar capillary column (see Fig. 2), where B group members have rising arrows and A group falling arrows.

suggesting that the support here had some influence on the solute. Camphor, another carbonyl compound, gave similar results. Of the more polar substances examined, the B1 citronellol and the B2 anethole gave comparable results on non-polar capillary and packed columns. With others, the capillary behaved as the equivalent of the packed column at temperatures about or above the 220°C limit previously used (*e.g.* menthol and pulegone).

Capillary columns gave a general contraction of the spread of $t_{R,rel}$ especially as the temperature increased. It is clearly important to use low temperatures for $t_{R,rel}$ determinations.

On the polar Carbowax 20M capillary the B1 citronellol and the A2 *iso*-menthone were the only substances giving results comparable to those obtained on the packed column. Some results again indicated that the capillary behaved as a high temperature extension of the packed column (*e.g.* A2 limonene and B3 carvone). In contrast, citronellyl acetate and camphor behaved as if the capillary were a *low* temperature extension of the packed column (Fig. 2).

From the present results, the low polarity A1 terpenyl acetates and A2 terpene

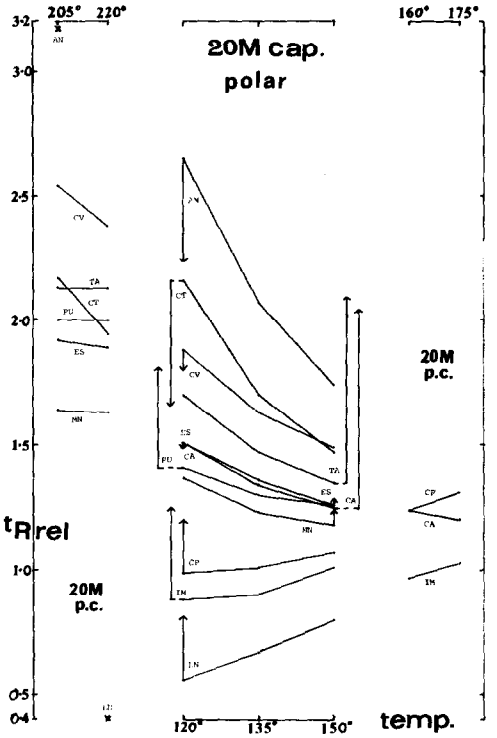

Fig. 2. Relative GC retention times (to linalool) plotted against corresponding temperatures of a polar polyethyleneglycol capillary (cap.)/packed column (p.c.). The present capillary results are shown centrally, with 1970 values[1] for the packed column on the left (high temperatures) and right (low temperatures). Abbreviations for the substances are given in Table I. Vertical arrows indicate the $t_{R,rel}$ for the same substance on the non-polar capillary column (see Fig. 1) where B group members have falling arrows and A group rising arrows.

hydrocarbon limonene are still clearly distinctive, having higher $t_{R,rel}$ values on the non-polar than on the polar capillary. Conversely, the B1 citronellol and the B2 anethole are polar enough to give much higher $t_{R,rel}$ on the polar capillary. However, other substances previously included in the B groups (camphor, menthol and pulegone) behaved on capillaries as though they belonged to group A, and are so classified in Table I. The capillary GC results confirmed the 1970 placement of *iso*-menthone in the low polarity group A2, rather than with other carbonyls. The aromatic estragole is not now assignable to either A or B groups.

Although, for $t_{R,rel}$ studies, capillary columns do not appear to be superior to packed columns, two capillary columns of differing polarity still enable a distinction to be made between compounds having virtually the same retention times on either a polar capillary (estragole and citronellyl acetate) or a non-polar capillary (carvone and pulegone; citronellyl and terpinyl acetates).

In studies of *Eucalyptus* leaf oils, the $t_{R,rel}$ method using packed columns has not been as effective as was hoped in identifying GC peaks. It now appears that the use of capillary columns will not improve this situation.

REFERENCE

1 P. N. Breckler and T. J. Betts, *J. Chromatogr.*, 53 (1970) 163.