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## Note

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### Gas chromatographic behaviour of trimethylsilyl derivatives of some monoterpenic alcohols and phenols found in volatile oils

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Monoterpene alcohols are significant components of some volatile oils, *e.g.* linalool in lavender, menthol in peppermint. Phenols of similar molecular size are important constituents of other oils, *e.g.* eugenol in clove, thymol in thyme. One chromatographic method of confirming the identity of such hydroxy-compounds is to note the change in their behaviour following derivatisation. This has previously been applied to a study of trimethylsilyl (TMS) derivatives of some monoterpenols by thin-layer chromatography<sup>1</sup>, but not by gas chromatography (GC).

TMS-phenol was first prepared in 1952<sup>2</sup>, but not for GC purposes. Rühlmann was the first to do this in 1961<sup>3</sup>, and he also prepared volatile derivatives of amino acids for GC<sup>4</sup>. TMS-derivatives were also prepared of solutes such as steroids<sup>5</sup> or pesticides<sup>6</sup> which were themselves volatile enough for GC. This was done to impart enhanced volatility, stability and decreased polarity to the test solutes, but Fishbein and Zielinski<sup>6</sup> also found that some elution values for the TMS derivatives (of pesticides) lie very close to those of the parent compounds and sometimes gave increased elution values on the non-polar column. This phenomenon has been confirmed by the present study.

#### EXPERIMENTAL

##### *Apparatus*

Pye 104 gas chromatograph, fitted with flame ionisation detector; hydrogen flow used 40 ml/min. Packed columns as detailed in Table I. Injector heater set at about 200°C. Mobile phase: purified nitrogen at 40 ml/min. Recorder: Perkin-Elmer 56.

##### *Materials*

Hydroxy-compounds: various commercial sources, and donations. Samples showed either no other GC impurity peaks, or only small ones.

Silanising reagents: "Tri-sil"<sup>®</sup> or N,O-bis(trimethylsilyl)acetamide from Pierce were used by adding 0.5 ml reagent to a small amount of test hydroxy-compound in a dry screw-capped glass vial, shaking it for 30 sec, then standing it on top of the warm GC oven for a few minutes. The TMS-derivatives were found to be stable at

TABLE I

RELATIVE RETENTION TIMES OF TMS-DERIVATIVES TO PARENT HYDROXY-COMPOUNDS, AND OF THESE TO MENTHOL

Columns at 120°C. Mobile phase: nitrogen at 40 ml/min.

<i>Packed columns used</i>						
<i>2% SP-2100 (methyl polysiloxane) on Chromosorb 80/100 in glass, 1.5 m × 4 mm I.D.</i>		<i>3% SP-2250 (phenyl-methyl (1:1) polysiloxane) on Supel- coport 100/120 in stain- less steel, 3.0 m × 5 mm I.D.</i>		<i>5% QF-1 (trifluoropropyl poly- siloxane) on Supelcoport 80/100 in glass, 1.5 m × 4 mm I.D.</i>		
<i>PA/LEC* for column</i>						
<i>-117</i>		<i>-11</i>		<i>+13</i>		
<i>TMS/OH**</i>	<i>OH/menthol</i>	<i>TMS/OH</i>	<i>OH/menthol</i>	<i>TMS/OH</i>	<i>OH/menthol</i>	
Geraniol	1.78	1.35	1.24	1.55	0.97	1.22
Eugenol	1.76	2.19	1.40	3.46	1.05	2.40
α-Terpineol	1.76	1.06	1.20	1.20	0.98	1.02
Linalool	1.70	0.75	1.26	0.67	1.02	0.77
Terpinen-4-ol	1.63	1.00	1.08	1.05	0.97	0.98
Citronellol	1.45	1.23	0.99	1.27	0.94	1.10
Menthol	1.40	1.00	0.96	1.00	0.95	1.00
Iso-borneol	1.33	0.94	0.83	1.00	0.83	1.00
Borneol	1.24	1.00	0.79	1.05	0.86	1.03
Thymol	1.11	1.52	0.75	2.08	0.83	1.40
<i>t<sub>R</sub></i> Menthol	2.5 min		5.0 min		1.5 min	

\* Average of six differences in retention indices for Linalool, Estragole and Carvone based on normal Paraffin series and normal Alcohol series against those determined on the SP-2250 column at 160°C in 1981<sup>7</sup>.

\*\* OH indicates (parent) hydroxy-compound: monoterpenol or C<sub>10</sub>-phenol.

room temperature (25–30°C) over several weeks. Both reagents worked equally well, but "Tri-sil" products contained a precipitate (ammonium chloride?). BSA mixtures gave a more complex solvent peak trace, which tended to overlap with TMS-derivatives of short retention time.

## RESULTS AND DISCUSSION

The results of subjecting eight monoterpenols and two C<sub>10</sub>-phenols (dissolved in ethanol) and their TMS-derivatives to GC on three columns of differing polarity are detailed in Table I.

The temperature of 120°C yielded solute retention times of 1–20 min. Work was restricted to various polysiloxane phases as these provide a suitable range of stationary phase polarities, whilst avoiding any chance of reaction with the excess silanising reagent present in the TMS-products.

Column polarities were rated on what is now called the PA/LEC scale used in this laboratory, described by Betts *et al.* in 1981<sup>7</sup> (see footnote to Table I). This relies

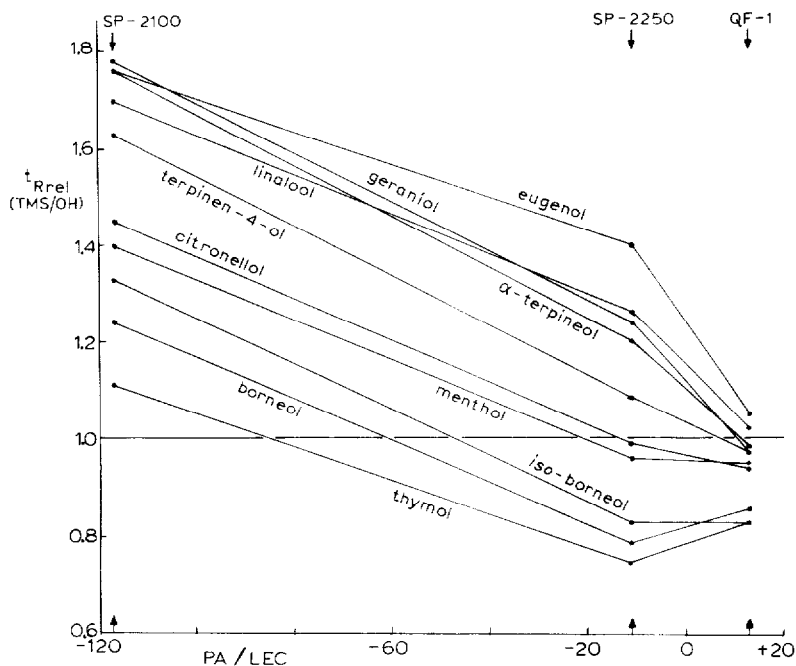


Fig. 1. Plot of relative retention times ( $t_{Rrel}$ ) for TMS-derivatives vs. parent hydroxy-compounds, against PA/LEC column polarity values (ref. 7).

on each laboratory designating its own standard column; in our case the SP-2250 one used in this work. The retention indices for the three probe solutes against *n*-alkanes and *n*-alcohols at 160°C on this column were originally determined in 1980; three years later, after considerable student use, they have only changed slightly, and are the same at 120°C.

Fig. 1 shows the effect of changing column polarity on the retention times of TMS-derivatives, relative to their parent compounds. On the most non-polar column (SP-2100), no TMS-derivative has a shorter retention time than its corresponding alcohol or phenol, and some are nearly 80% increased. With such a column, silanising these hydroxy-compounds does *not* shorten their retention times, probably because the lowered polarity of the TMS-derivatives makes them a better match for the stationary phase. This confirms the observation of Fishbein and Zielinski<sup>6</sup>. For a QF-1 column, they found variable results, and it can be seen from Fig. 1 that this is due to a general lowering of the relative retention values on this more polar column, so that many of the solutes studied now show a decrease in retention time upon silanising. However, there is a considerable compaction of the values, which all appear likely to become approximately 0.9 on a theoretical column with a PA/LEC value of about +25.

On the SP-2250 column, of intermediate polarity between the other two, half the ten compounds studied show a decrease in retention time upon silanisation. Presumably TMS-thymol and -borneol are the most polar (least non-polar) derivatives, as suggested by their increasing retention times (relatively) once the column becomes somewhat polar (QF-1).

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