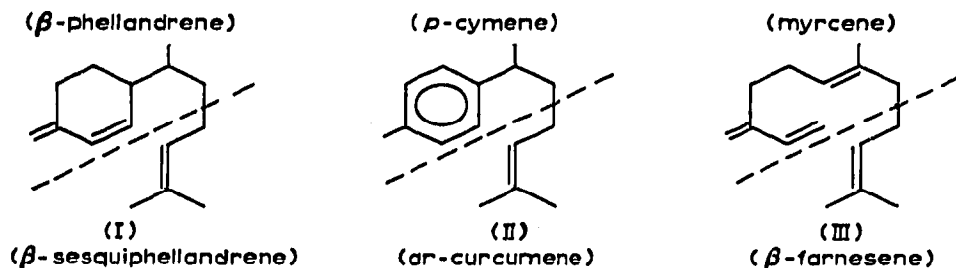## Notes

CHROM. 4358

A guide for the prediction of the gas chromatographic retention times of selected sesquiterpenes

During recent studies on essential oils[1] it has been found that the most readily available characteristic of a sesquiterpene is its gas chromatographic retention time since this can usually be measured from a crude mixture. In some cases a considerable amount of useful information can be derived from this property alone by correlation with the retention times of known monoterpenes.

Examination of the structures of sesquiterpenes based on the bisabolane and farnesane skeletons reveals that each can be regarded as a monoterpene extended by an isoprene unit attached to the isopropyl or isopropylidene grouping, e.g. I, II and III.

(β-phellandrene)   (p-cymene)   (myrcene)

(I)   (II)   (III)
(β-sesquiphellandrene)   (ar-curcumene)   (β-farnesene)

This addition of a uniform increment to each of the monoterpenes would be expected to increase the gas chromatographic retention times in a consistent way. Thus ideally the retention times of the sesquiterpenes can be regarded as being made up of two contributions: (1) a variable contribution arising from the monoterpene unit and (2) a consistent contribution from the additional isoprene unit. In consequence it may be expected that the customary semi-log plot of retention times versus carbon number[2] if applied to terpene–sesquiterpene pairs will yield approximately parallel lines (see Fig. 1).

The data for a number of known mono- and sesqui-terpenes was plotted in this fashion giving lines which were found to be approximately parallel. Therefore if a plot is made for one corresponding pair the retention times for other sesquiterpenes can be derived. Lines constructed parallel to the known reference line and passing through the retention times of the known monoterpenes will intersect the sesquiterpene line at approximately the retention times of the corresponding sesquiterpenes (see Fig. 2). Most satisfactory results are obtained by using a reference pair as closely related as possible to the sesquiterpene, the retention time of which is to be predicted.

A comparison between predicted and observed retention times is shown in Table I. The close correlation obtained indicates that for these selected sesquiterpenes this relationship can be used to obtain approximate retention times from those of corresponding monoterpenes. In addition it suggests that a similar relationship would probably exist between analogous structurally related monoterpene–sesquiterpene
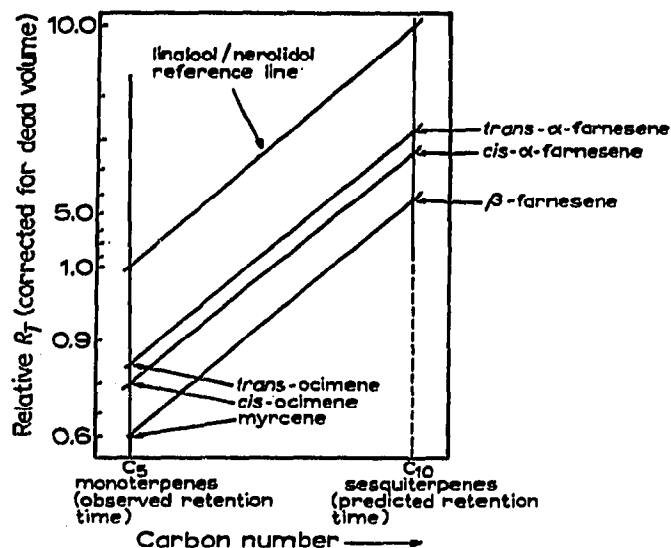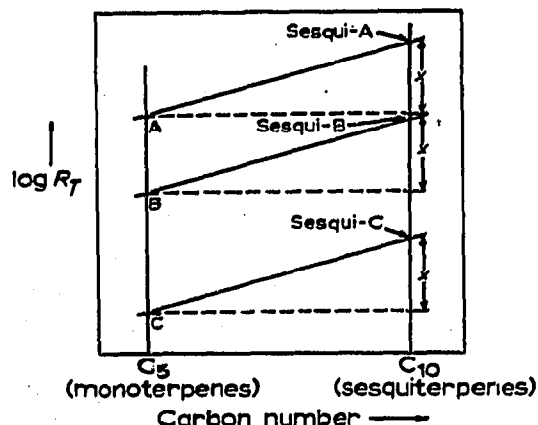
Fig. 1. Hypothetical plots of the retention times of mono- and sesquiterpenes. The retention times of A, B and C represent the variable contributions while x represents the consistent contribution from the additional isoprene unit.

Fig. 2. Plot used to predict the retention times of acyclic sesquiterpenes.

groups, e.g. camphene–β-santalene and α-pinene–α-bergamotene. However, it should be noted that information obtained in this way cannot be regarded as conclusive but as a useful guide for isolation procedures or for further work aimed at a positive identification or structural characterisation.

Experimental

Gas chromatography. An Aerograph Model A-600-B instrument incorporating a

TABLE I

OBSERVED AND PREDICTED SESQUITERPENE RETENTION TIMES
Corrected for dead volume.

Monoterpene used for primary retention time	Sesquiterpene	Retention times	
		Predicted	Observed
Monocyclic group[a]			
β-Phellandrene	β-sesquiphellandrene	10.4	10.4
Limonene	β-bisabolene	9.2	9.5
Terpinolene	γ-bisabolene	12.4	—
Terpineol-4	anymol	23.4	22.0
Acyclic group[b]			
Myrcene	β-farnesene	6.0	6.0
cis-Ocimene	cis-α-farnesene	7.8	7.8
trans-Ocimene	trans-α-farnesene	8.6	8.4

[a] Calculated from a zingiberene–α-phellandrene reference line; retention times relative to α-phellandrene = 1.

[b] Calculated from a linalool–nerolidol reference line, see Fig. 1; retention times relative to linalool = 1.

flame ionisation detector and fitted with stainless steel columns (6 ft. × ⅛ in.) was used. The column packing was Gas-Chrom 80–100 mesh size containing 15% by weight of Apiezon M. A column temperature of 170° was maintained while nitrogen was used as carrier gas.

Terpenoid samples. β-Sesquiphellandrene and β-bisabolene were contained in fractions from the chromatography on silver nitrate treated alumina (234 g containing 34% silver nitrate) of distillation fractions (b.p. 89–90.5° at 1.0 mm) from the essential oil of ginger. Benzene in hexane (1:5) was used as eluant. Purity was demonstrated by the usual spectroscopic and chromatographic procedures and by satisfactory combustion analyses.

Nerolidol (75 ml) in pyridine (375 ml) was added to phosphorus oxychloride (150 ml) in pyridine (375 ml) and allowed to stand for 48 h then heated at 100° for 1 h. Subsequent working up yielded a yellow oil containing two major products. These were separated using an Auto-Prep Model 705 preparative gas chromatograph fitted with a 20 ft. × ⅜ in. column packed with 20% Apiezon M on Gas-Chrom. Satisfactory combustion analyses combined with close ultraviolet, infrared and proton magnetic resonance spectral correlations with results reported in the literature[3–5] revealed these compounds to be *trans*-α-farnesene and β-farnesene. Another compound present was tentatively identified as *cis*-α-farnesene.

Food Preservation Research Laboratory, D. W. CONNELL
Queensland Department of Primary Industries,
Hamilton, Brisbane (4007),
Queensland (Australia)

1 D. W. CONNELL AND M. D. SUTHERLAND, *Australian J. Chem.*, 19 (1966) 283.
2 A. T. JAMES AND A. J. P. MARTIN, *Biochem. J.*, 50 (1952) 679.
3 Y. R. NAVES, *Helv. Chim. Acta*, 49 (1966) 1029.
4 T. NORIN, *Acta Chem. Scand.*, 19 (1965) 1020.
5 G. OHLOFF, J. SEIBL AND E. KOVATS, *Ann. Chem.*, 695 (1964) 84.