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## Note

# Polyphenyl ether, a liquid phase for the gas chromatographic–mass spectrometric analysis of monoterpene hydrocarbons

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Only a few papers describing liquid phases for the gas chromatographic separation of the monoterpene hydrocarbons have appeared in the literature[1–4] and most of these liquid phases have been used to separate only a limited number of the naturally occurring monoterpenes. The gas chromatographic–mass spectrometric (GC–MS) analysis of the trace levels (ppb*) of organic compounds volatilized by plants[5] requires a liquid phase which provides good resolution of a large number of these monoterpenes. The separation of 20 monoterpene hydrocarbons has been reported on packed columns coated with $\beta,\beta'$-oxydipropionitrile (ODPN)[1]. Packed columns coated with this phase contribute significantly to mass-spectrometer background during GC–MS analysis and in order to minimize this problem these columns must be operated isothermally at 70° or lower, which results in longer retention times and broad peaks for the higher-boiling compounds. Additionally, the sensitivity of the MS analysis is reduced by broad GC peaks.

Polyphenyl ether (6 rings) is a liquid phase which has been found to be excellent for the GC–MS analysis of the monoterpene hydrocarbons. Capillary columns coated with this phase will not contribute to mass-spectrometer background when operated at 150° and can be used in temperature-programmed analysis to give sharp peaks thus increasing the MS sensitivity.

## MATERIALS AND METHODS

Most of the monoterpene hydrocarbons used in this study were obtained from the ether extract of the steam distillate of leaves of *Lepechinia calcyina*. Cyclofenchene and α- and β-fenchene were obtained by the dehydration of fenchyl alcohol[6]. Samples of *allo*-ocimene and santene were generously supplied by R. A. Rasmussen and E. Zavarin, respectively. The monoterpenes were separated using a 50 ft. × 0.02 in. I.D. support coated open tubular (SCOT) column (Perkin Elmer, Norwalk, Conn., U.S.A.) coated with polyphenyl ether (6 rings). The conditions for the chromatographic analysis are given in Fig. 1. The terpenes were identified by comparing their

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* The American billion ($10^9$) is meant.

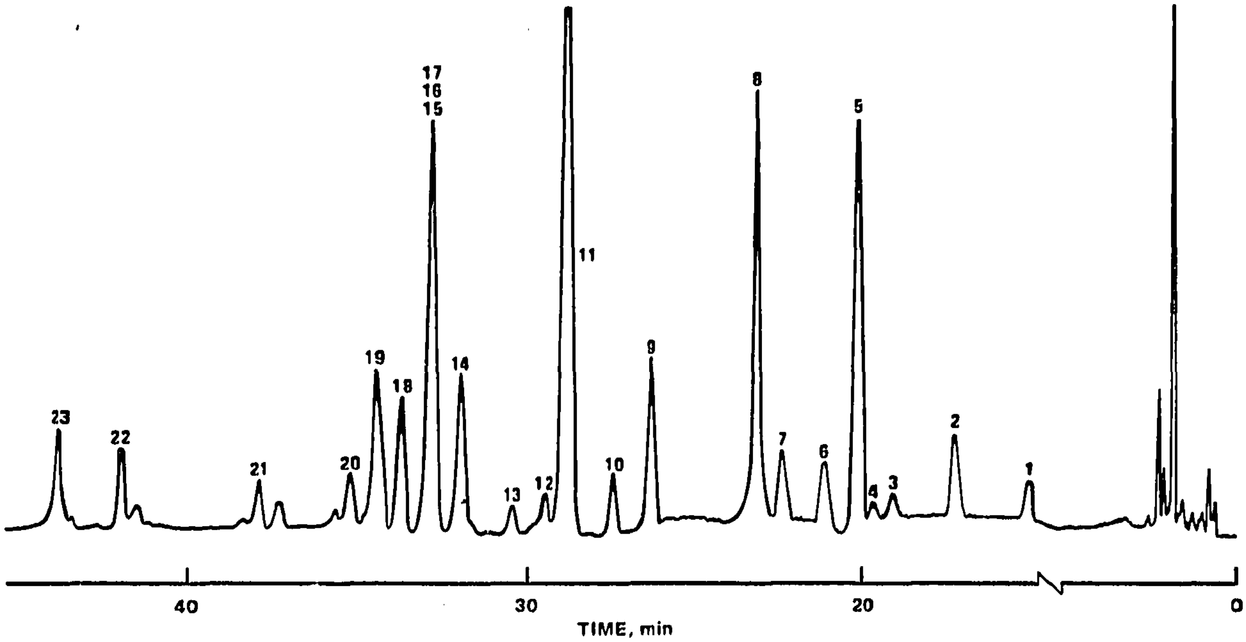

Fig. 1. Mass spectrometer total ion current monitor chromatogram of 23 monoterpene hydrocarbons. 50 ft. × 0.02 in. SCOT column coated with polyphenyl ether (6 rings). Temperature programme: 8 min at 60°, 60 to 150° at 2°/min. Helium flow-rate, 3 ml/min. Numbers as in Table I.

TABLE I

RETENTION TIMES OF TERPENE HYDROCARBONS RELATIVE TO THAT OF LIMONENE

| *No.* | *Compound* | *Retention time (limonene = 1000)* |
|---|---|---|
| 1 | Cyclofenchene | 469 |
| 2 | Santene | 539 |
| 3 | Tricyclene | 597 |
| 4 | $\alpha$-Thujene | 614 |
| 5 | $\alpha$-Pinene | 627 |
| 6 | $\beta$-Fenchene | 659 |
| 7 | $\alpha$-Fenchene | 702 |
| 8 | Camphene | 722 |
| 9 | $\beta$-Pinene | 822 |
| 10 | Mrycene | 857 |
| 11 | $\Delta^3$-Carene | 899 |
| 12 | $\alpha$-Phellandrene | 922 |
| 13 | $\alpha$-Terpinene | 952 |
| 14 | Limonene | 1000 |
| 15 | Sabinene | 1028 |
| 16 | $\beta$-Phellandrene | 1028 |
| 17 | $\beta$-Ocimene-x | 1028 |
| 18 | $\beta$-Ocimene-y | 1058 |
| 19 | Cymene | 1078 |
| 20 | $\gamma$-Terpinene | 1103 |
| 21 | Terpinolene | 1188 |
| 22 | *allo*-Ocimene (*trans–cis*?) | 1313 |
| 23 | *allo*-Ocimene (*trans–trans*?) | 1366 |

mass spectra with those previously published[7,8]. The GC–MS system used in the analysis has been previously described[9].

## RESULTS AND DISCUSSION

Fig. 1 is a mass spectrometer total ion current monitor chromatogram showing the separation of the monoterpene hydrocarbons. The relative retention times of the monoterpenes are given in Table I. The retention times of the monoterpenes not present in the oil of *Lepechinia calcyina* were determined relative to limonene under the same conditions as indicated in Fig. 1.

As shown in Fig. 1, 21 monoterpene hydrocarbons can be separated using polyphenyl ether, and the monoterpenes are well separated except for $\beta$-phellandrene, sabinene and $\beta$-ocimene-x. The isomers of *allo*-ocimene are separated but cannot be identified because they have identical mass spectra[7]. $\beta$-Phellandrene, sabinene and $\beta$-ocimene-x cannot be separated on polyphenyl ether, but compared to $\beta,\beta'$-oxydipropionitrile, polyphenyl ether is superior for the separation of $\alpha$-terpinene from limonene and $\beta$-ocimene-y from terpinolene, and improves the separation of tricyclene from $\alpha$-pinene.

The sensitivity of the MS analysis is increased by a factor of about 1.5–2 for $\alpha$-terpinene, $\beta$-ocimene-x and -y, terpinolene, and cymene on polyphenyl ether (SCOT column) compared to $\beta,\beta'$-oxydipropionitrile (SCOT column) and by a factor of about 4 for the *allo*-ocimenes. In addition to the advantages of polyphenyl ether for the GC–MS analysis of the monoterpene hydrocarbons, the retention times of the terpenes are markedly different from those on $\beta,\beta'$-oxidipropionitrile so that the two phases provide a good means of compound identification based on retention times.

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