

## Note

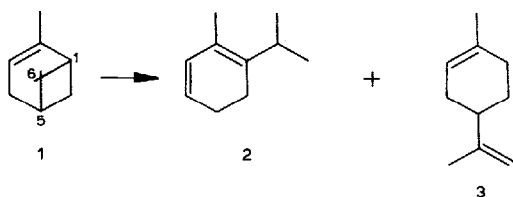
### Gas-liquid chromatographic separation of saturated terpene hydrocarbons using glass capillary columns

V. V. BAZYL'CHICK\*, E. A. MISTRYUKOV, P. I. FEDOROV and K. V. BELYAEVA

Department of Organic Chemistry, Chuvash State Uljanov University, 428015 Cheboksary (U.S.S.R.)

(First received November 7th, 1983; revised manuscript received January 10th, 1984)

The catalytic hydrogenation of terpene hydrocarbons and related compounds under mild conditions (room temperature, 1 bar) leads to saturated derivatives that are much less prone than the parent compounds to undergo skeletal rearrangements. Owing to their thermal stability, these saturated terpenes are especially suitable for study by high-performance gas-liquid chromatography (GLC), allowing the accurate determination of the chemical composition of essential oils. Such a procedure can also be useful for monitoring some semi-synthetic processes, *e.g.*, the recycling and processing of labile pinane- and carane-type derivatives. Of particular interest in this respect is the cleavage of the cyclobutane ring in  $\alpha$ -pinene (1), between C-5 and C-6, leading to *o*-menthane derivatives (*e.g.*, 2), some representatives of which occur naturally<sup>1</sup> and have recently been found to be effective plant-growth regulators<sup>2-4</sup>.

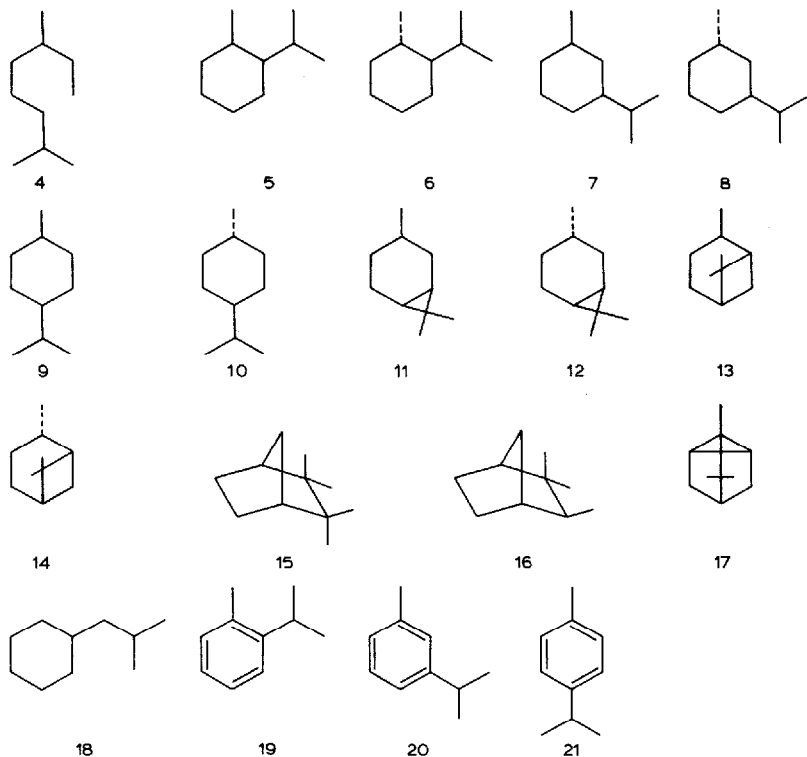


However, in contrast to the widely used<sup>5,6</sup>, alternative preparation of *p*-menthane derivatives (*e.g.*, 2) from  $\alpha$ -pinene, only one process affording *o*-menthane-type compounds has hitherto appeared in the literature, namely the production of 1,5-*o*-menthadiene (2) from 1<sup>7</sup>. There is little doubt that the lack of convenient analytical procedures for investigating complex mixtures of mono- and bicyclic terpene isomers has contributed to this situation.

We have previously attempted to separate isomeric hydrocarbons belonging to the camphane, pinane, carane, *o*, *m*- and *p*-menthane, isobutylicyclohexane and 1,1,4-trimethylcycloheptane series, using packed, metallic columns (6 m  $\times$  4 mm I.D.) and three polarity-contrasted stationary phases [squalane, cyanopolysiloxane XE-60 and tris(2-cyanoethoxy)propane]<sup>8</sup>. In all these separations, however, a significant number of compounds displayed very similar retention times ( $t_R$ ) values and gave overlapping peaks. For instance, five hydrocarbons had  $t_R$  ranging from 0.87

to 0.89 (relative to *p*-cymene) on squalane, six had  $t_R = 0.40-0.43$  on cyanopolysiloxane XE-60 and eight had  $t_R = 0.13-0.15$  on tris(2-cyanoethoxy)propane.

In this paper, we describe the application of three glass capillary columns coated with PEG-40M and silicones XE-60 and OV-101 and one metallic column coated with XE-60 to the separation of the following hydrocarbon mixture: 2,6-dimethyloctane (4), *cis*- (5) and *trans*-*o*-menthane (6), *cis*- (7) and *trans*-*m*-menthane (8), *cis*- (9) and *trans*-*p*-menthane (10), *cis*- (11) and *trans*-carane (12), *cis*- (13) and *trans*-pinane (14), 2,2,3-*endo*- (15) and -*exo*-trimethylbicyclo[2.2.1]heptane (16) (*endo*- and *exo*-isocamphane), tricyclene (17), isobutylcyclohexane (18) and *o*- (19), *m*- (20) and *p*-cymene (21).



## EXPERIMENTAL

Separations on glass capillary columns (55 m  $\times$  0.25 mm I.D.) were carried out with a Biochrom-1 gas chromatograph (U.S.S.R.). The columns were made from Pyrex glass tubing using a glass capillary stretching stand designed by the Special Designing Bureau of Organic Chemistry Institute of the U.S.S.R. Academy of Sciences<sup>9</sup>.

Adequate coating of the columns with 0.0156 mg/cm<sup>2</sup> of the stationary phases (PEG-40M, XE-60 and OV-101) was ensured by the high-pressure static method described earlier<sup>10</sup>, after pickling<sup>11,12</sup> of the inner glass surface. Thus, 6 ml of 1% hydrofluoric acid solution, 3 ml of distilled water, 3 ml of a 1% solution of potassium

hydroxide in methanol and 3 ml of freshly distilled methanol were successively forced through the columns under a pressure of 5 bar of argon. After complete drying by blowing argon through at 20–25°C, the columns were filled with a 0.25% solution of stationary phase in a suitable solvent and sealed at one end. Finally, the solvent was removed at 200°C using the device employed for the introduction of the solution of the stationary phase.

The efficiency of the columns prepared in this way reached 3460 theoretical plates per metre for dodecane (calculated from five parallel tests). The separations of hydrocarbon mixtures were carried out at 70°C with nitrogen as carrier gas (inlet pressure 1.7 bar), with the injection port and flame-ionization detector heated at 250°C.

The metal capillary column used in some experiments (50 m × 0.2 mm I.D.) was made of stainless steel and coated with cyanopolysiloxane XE-60. The separations were carried out on a Chrom-31 gas chromatograph (Czechoslovakia).

## RESULTS

The chromatograms obtained with the glass capillary columns are shown in

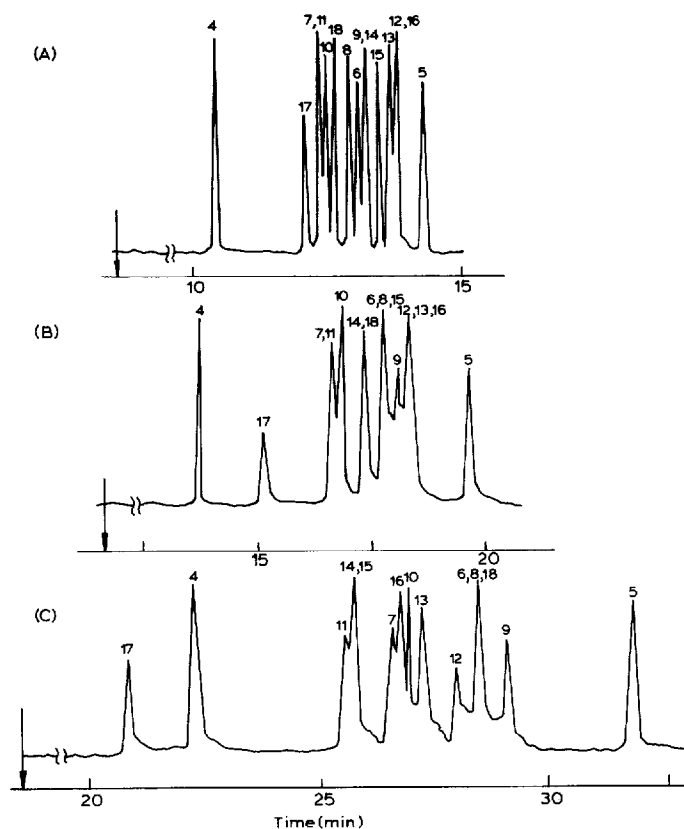


Fig. 1. GLC separations of saturated terpene hydrocarbons using glass capillary columns. Stationary phases: (A) PEG-40M; (B) XE-60; (C) OV-101.

TABLE I

RETENTION TIMES OF SATURATED TERPENE HYDROCARBONS AND CYMENES RELATIVE TO *trans-p*-MENTHANE

Hydrocarbon	Stationary phase			
	PEG-30M (glass column)	OV-101 (glass column)	XE-60 (glass column)	XE-60 (metallic column)
2,6-Dimethyloctane (4)	0.52	0.75	0.59	—
Tricyclene (17)	0.91	0.67	0.78	0.89
<i>cis</i> -Carane (11)	0.98	0.92	0.98	1.07
<i>cis-m</i> -Menthane (7)	0.98	0.97	0.98	—
<i>trans-p</i> -Menthane (10)	1.00	1.00	1.00	1.00
Isobutylicyclohexane (18)	1.04	1.07	1.06	—
<i>trans-m</i> -Menthane (8)	1.11	1.07	1.12	—
<i>trans-o</i> -Menthane (6)	1.13	1.07	1.12	1.05
<i>cis-p</i> -Menthane (9)	1.17	1.10	1.16	1.06
<i>trans</i> -Pinane (14)	1.17	0.93	1.06	1.05
<i>endo</i> -Isocamphane (15)	1.24	0.93	1.12	1.06
<i>cis</i> -Pinane (13)	1.29	1.01	1.19	1.07
<i>trans</i> -Carane (12)	1.32	1.05	1.19	1.07
<i>exo</i> -Isocamphane (16)	1.32	0.99	1.19	1.07
<i>cis-o</i> -Menthane (5)	1.43	1.25	1.36	1.17
<i>m</i> -Cymene (20)	5.48	1.29	2.88	—
<i>p</i> -Cymene (21)	5.56	1.32	2.90	1.89
<i>o</i> -Cymene (19)	6.80	1.44	3.58	2.18

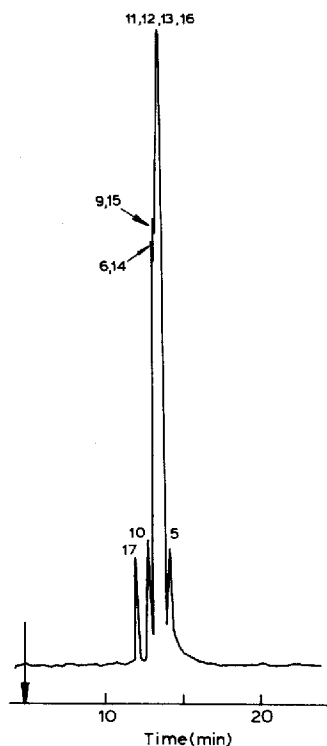


Fig. 2. GLC separation of saturated terpene hydrocarbons using a metal capillary column coated with XE-60.

Fig. 1 and the corresponding  $t_R$  relative to *p*-cymene (21) are listed in Table I (the smallest  $\Delta t_R$  needed for peak separation was 0.01). As is apparent from Fig. 1, the investigated hydrocarbon mixture, which is similar to mixtures expected to arise from ring cleavage and catalytic hydrogenation of 3-carene and of  $\alpha$ -pinene (1) and  $\beta$ -pinene, was not completely resolved on any of the three stationary phases tried. The best result was obtained on PEG-40M, although the following pairs of compounds were not separated: (7) and (11), (9) and (14) and (12) and (16). These pairs could be resolved on OV-101 (Fig. 1C), but only at the expense of other separations. Alternatively, the separation of the same hydrocarbon mixture on a metallic capillary column coated with XE-60 proved unsatisfactory (Fig. 2). In comparison, the glass capillary column coated with the same stationary phase allowed the complete separation of *trans*-*o*-menthane (6), *trans*-pinane (14), *cis*-*p*-menthane (9) and *exo*-isocamphane (16), but *cis*-pinane (13), *trans*-carane (12) and *endo*-isocamphane (15) appeared together as a single, symmetrical peak (Fig. 1B).

The results show that glass capillary columns have distinct advantages for the application studied, making possible the identification of individual hydrocarbons in the menthane and cymene series, and allowing their separation from bicyclic isomers such as the stereoisomeric pinanes and isocamphanes.

#### ACKNOWLEDGEMENT

We are grateful to Dr. V. P. Chizhkov for valuable advice.

#### REFERENCES

- 1 G. Snatzke, A. F. Thomas and G. Ohloff, *Helv. Chim. Acta*, 52 (1969) 1253.
- 2 V. V. Bazyl'chick, V. V. Anisimov, P. S. Smirnov and A. S. Abrukov, *XIIIth Mendeleev Congress on General and Applied Chemistry, Abstracts of Reports and Presentation, No. 6, Problem of Agricultural Chemistry*, Nauka, Moscow, 1981, p. 151.
- 3 V. V. Bazyl'chick and V. V. Anisimov, *All-Union Conference on Chemical Means of Plant Protection. Section 4, Synthesis and Testing of Biologically Active Compounds*, U.S.S.R. Academy of Sciences, Ufa, 1982, p. 120.
- 4 V. V. Anisimov and V. V. Bazyl'chick, *IXth International Congress on Essential Oils, Abstracts of Reports and Presentations*, Singapore, 1983, p. 30.
- 5 Y. R. Naves, *Usp. Khim.*, 37 (1968) 1815; *C.A.*, 70 (1969) 29066g.
- 6 A. F. Thomas, in J. ApSimon (Editor), *The Total Synthesis of Natural Products*, Vol. 2, Wiley, New York, 1973, pp. 1-95.
- 7 H. Kojima, *Nippon Kagaku Zasshi*, 82 (1961) 115; *C.A.*, 56 (1962) 10193b.
- 8 V. V. Bazyl'chick and P. I. Fedorov, *J. Anal. Chem. U.S.S.R.*, 38 (1983) 356.
- 9 E. A. Mistryukov, L. S. Savichev and V. V. Gavrilov, *Czechoslovak Chemical Society Chromatography Groups. Progress in Chromatography (2nd Danube Symposium)*, Carlsbad, Czechoslovakia, 1979, p. 18.
- 10 E. L. Tekova and E. A. Mistryukov, *Chromatographia*, 4 (1971) 77.
- 11 R. V. Golovnya, E. A. Mistryukov and A. L. Samusenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7 (1977) 1632.
- 12 M. S. Vydgergauz, A. A. Martynov, S. K. Lezina and E. I. Gurchenko, *Chemistry and Technology of Fuels and Oils*, Nauka, Moscow, 1972, pp. 10 and 55.