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Note

Gas-liquid chromatographic study of monoterpene hydrocarbons of conifer balsams and ring opening products of pinane and carane structure

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Coniferous trees (pine, spruce, cedar, fir, larch) represent 40% of all forests in the temperate zone. They produce balsams (oleoresins) of complex composition, whose major volatile fraction, called turpentine¹, is made up of monoterpene hydrocarbons. Typically, turpentine contains alloocimene (1), myrcene (2), sylvestrene (3), *m*-1,3(8)-menthadiene (4), α - (5) and γ -terpinene (6), α - (7) and β -phellandrene (8), limonene (9), terpinolene (10), α - (11) and β -pinene (12), 3-carene (13), camphene (14), santene (15), tricyclene (16) and *p*-cymene (17)²⁻⁶.

As balsams contain monoterpene hydrocarbons in addition to resin acids, *o*-menthane derivatives resulting from acid-catalysed ring-cleavage reactions of pinane-type terpenes can be expected to occur in turpentine. Those *o*-menthane representatives formed by cleavage of the C(5)-C(6) bond⁷ in α -pinene (11) are of particular interest, because they are plant growth promoters^{8,9}.

A precise investigation of the mono- and bicyclic terpene hydrocarbons present in coniferous balsams was made possible using a recently developed procedure, in which catalytic hydrogenation under mild conditions (room temperature, atmospheric pressure) is combined with highly efficient gas-liquid chromatographic (GLC) separations of the mixtures of saturated, thermostable monoterpenes thus produced^{10,11}.

In this work, we studied the GLC separation of the terpene hydrocarbons resulting from the catalytic hydrogenation of soft resin samples of fir (*Abies sibirica* L.) and common pine tree (*Pinus sylvestris* L.), and oleoresinous turpentine, using glass capillary columns coated with PEG 40M and silicones XE-60 and OV-101, respectively. We also examined the hydrogenation products of some semi-synthetic mixtures, such as those formed by pyrolysis and catalytic vapour-phase reactions of α - (11) and β -pinene (12), and of various turpentine. All these hydrogenated mixtures were expected to contain 2,6-dimethyloctane (18), *cis*- (19) and *trans*-*o*-menthane (20), *cis*- (21) and *trans*-*m*-menthane (22), *cis*- (23) and *trans*-*p*-menthane (24), *cis*- (25) and *trans*-carane (26), *cis*- (27) and *trans*-pinane (28), *endo*- (29) and *exo*-2,2,3-trimethylbicyclo [2.2.1]heptane (30), isobutylcyclohexane (31), *o*- (32), *m*- (33) and *p*-cymene (17) and isobutylbenzene (34).

EXPERIMENTAL

The separations were carried out on a Biochrom-1 (U.S.S.R.) gas chromatograph, using a Pyrex glass capillary stretching stand designed by the Special Designing Bureau of the Organic Chemistry Institute, U.S.S.R. Academy of Sciences^{1,2}.

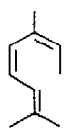
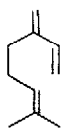
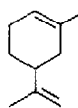
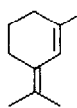
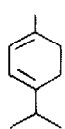
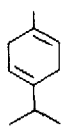
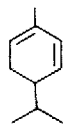
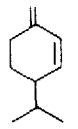
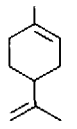
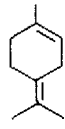
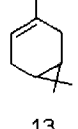
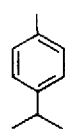
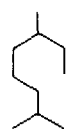
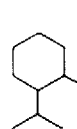
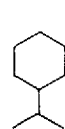
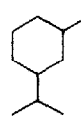
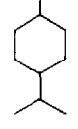
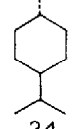
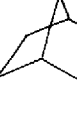
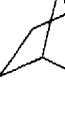
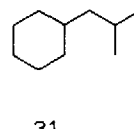
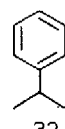
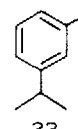
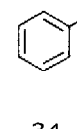
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TABLE I

GLC ANALYSIS OF THE MONOTERPENE FRACTION FROM HYDROGENATED OLEORESINS AND TURPENTINE

All values are in wt in %.

Product hydrogenated	<i>cis</i> -Pinane (27)	<i>trans</i> -Pinane, <i>endo</i> -2,2,3-tri-methylbicyclo-[2,2,1]heptane (28,29)	<i>cis</i> -Carane (25)	<i>trans</i> -Carane (26)	<i>exo</i> -2,2,3-Trimethylbicyclo[2,2,1]-heptane (30)	<i>cis</i> - <i>o</i> -Menthane (19)
Oleoresin from <i>Pinus silvestris</i> L.	43.4	16.4	5.2	20.8	0.7	—
Oleoresin from <i>Pinus silvestris</i> L. obtained using 2,4-dichlorophenoxyacetic acid	57.0	20.8	2.5	11.2	0.3	—
Oleoresin from <i>Abies sibirica</i> L.	38.8	13.5	2.2	2.3	17.5	—
Turpentine from <i>Pinus silvestris</i> L.	48.7	23.4	5.9	9.7	0.5	—
<i>GLC analysis of the hydrogenated products from vapour-phase isomerization reactions on diatomite at 350°C (time of the contact 50 sec):</i>						
α -Pinene	41.0	4.2	—	—	—	0.3
β -Pinene	40.4	2.0	—	—	—	0.4
Turpentine from <i>Pinus silvestris</i> L.	—	2.3	1.6	3.9	7.6	0.1
Turpentine extracted from pine tree stumps	—	6.6	17.2	1.3	2.2	1.8
Turpentine obtained in cellulose production	—	0.6	3.3	2.9	2.5	0.8
α -Pinene pyrolysis product	3.6	2.4	—	—	1.6	—
<i>GLC analysis of the hydrogenated products from vapour-phase isomerization reactions on Zeolite KX at 200°C (time of contact 50 sec):</i>						
α -Pinene	25.0	12.3	—	—	8.7	—
β -Pinene	23.2	7.8	—	—	3.3	—
<i>GLC analysis of the hydrogenated products of vapour-phase conversion of terpenes under the action of Al₂O₃ impregnated with NH₃ at 350°C (time of contact 50 sec):</i>						
α -Pinene	2.5	8.6	—	—	21.2	—
β -Pinene	—	6.1	—	—	19.8	0.1

<i>trans-o-menthane, trans-m-menthane, isobutylcyclohexane (20,22,31)</i>	<i>cis-m-Menthane (21)</i>	<i>cis-p-Menthane (23)</i>	<i>trans-p-Menthane (24)</i>	<i>2,6-Dimethyloctane (18)</i>	<i>Tricyclene (16)</i>	<i>Isobutylbenzene (34)</i>	<i>o-Cymene (32)</i>	<i>m-Cymene (33)</i>	<i>o-Cymene (17)</i>	<i>Not identified</i>
—	2.8	5.6	1.6	0.1	—	—	—	—	1.2	2.2
—	2.4	2.5	1.4	0.1	—	—	—	—	0.6	1.2
—	9.0	12.9	1.0	1.9	—	—	—	—	0.6	0.3
—	3.9	3.7	2.1	0.1	—	—	—	—	1.2	0.8
0.8	12.0	11.6	1.6	3.3	—	0.4	—	—	20.0	5.2
—	8.8	6.3	1.4	3.5	—	0.7	—	—	15.0	21.3
0.8	17.3	45.5	3.9	2.6	—	0.3	0.7	—	8.1	4.7
0.6	13.9	27.6	1.6	0.4	0.9	1.3	1.1	—	9.4	13.6
1.7	12.5	25.4	5.8	2.9	0.4	0.4	2.1	—	22.5	15.8
—	13.0	35.2	28.8	0.5	—	—	—	—	4.3	10.6
—	12.1	32.0	—	1.2	—	—	—	—	7.1	1.6
—	19.0	19.6	1.5	3.0	—	—	—	—	9.9	12.4
.9	—	11.0	24.8	1.5	9.2	—	—	—	4.9	15.4
.4	—	10.2	34.7	1.2	5.8	—	0.1	—	5.8	16.8

Adequate coating of the columns with 0.0156 mg/cm² of each stationary phase (PEG 40M, XE-60 and OV-101) was ensured by using the high-pressure static method described earlier¹³⁻¹⁵, after pickling of the inner glass surface^{13,14}. The columns prepared in this way had an efficiency of 3460 theoretical plates per metre for dodecane (as calculated from five parallel determinations). The mixtures of hydrocarbons were separated at 70°C with nitrogen as the carrier gas (inlet pressure 1.7 bar; injection port and flame-ionization detector held at 250°C).

RESULTS

The results in Table I show that the major terpene hydrocarbons that occur in various soft resin samples from pine tree, fir and turpentine from pine tree belong to the pinane, carane and *p*-menthane series. Small amounts (1-2%) of acyclic terpenes are also present but, contrary to the work of Bardyshev and co-workers^{16,17}, no *m*-menthane-type compounds could be detected. Similarly, no *o*-menthane was found in the hydrogenated mixtures¹⁸ (*o*-menthane derivatives are not produced by either α -pinene (11) pyrolysis vapour-phase isomerization of α - (11) and β -pinene (12) on zeolite KX, although they are formed in small amounts in the presence of diatomite¹⁹ or aluminium oxide impregnated with ammonia²⁰).

Our results demonstrate that the use of glass capillary columns allows the efficient separation of mixtures of isomeric and/or stereoisomeric menthanes, pinanes, caranes, *exo*- and *endo*-2,2,3-trimethylbicyclo[2.2.1] heptanes and cymenes even in the presence of 2,6-dimethyloctane (18), isobutylcyclohexane (31) and isobutylbenzene (34). This constitutes a convenient way of studying the composition of natural or semi-synthetic mixtures of monoterpene hydrocarbons via catalytic hydrogenation.

REFERENCES

- 1 I. I. Bardyshev and E. P. Donzova, in I. I. Bardyshev (Editor), *Synthetic Products from Rosin and Turpentine*, Volgo-Vyatsk Publishing House, Gorki, 1970, p. 36.
- 2 W. Zandermann, *Natural Resins, Turpentine, Tall Oils (Chemistry and Technology)*, Lesnaya Promyshlennost Publishing House, Moscow, 1964, p. 51.
- 3 G. Dupont, *Turpentine*, SSTEP, Leningrad, 1931.
- 4 E. Gildemeister and F. Hoffman, *Ätherischen Öle Riechst. Parfüm. Essenzen Aromen*, 4 (1956) 204.
- 5 N. T. Mirov, *Composition of Gum Turpentine of Pines*, *Tech. Bull.*, 1961, No. 1239.
- 6 I. I. Bardyshev, A. N. Boulgakov, E. P. Donzova, R. I. Zhen'ko and A. L. Perzovski, in N. A. Borysevitch (Editor), *Belorussian Soviet Encyclopaedia*, Belorussian Academy of Sciences, Minsk, 1979, p. 345.
- 7 H. Kojima, *Nippon Kagaku Zasshi*, 82 (1961) 115; *C.A.*, 56 (1962) 10193b.
- 8 V. V. Bazyl'chick, V. V. Anisimov, P. S. Smirnov and A. S. Abrukov, *XII Mendeleev Congress on General and Applied Chemistry, Abstracts of Reports and Presentation, No. 6, Problems of Agricultural Chemistry*, Nauka, Moscow, 1981, p. 151.
- 9 V. V. Anisimov and V. V. Bazyl'chick, *IXth International Congress of Essential Oils, Singapore, Abstracts of Reports and Presentation*, 1983, p. 30.
- 10 V. V. Bazyl'chick, E. A. Mistryukov, P. I. Fedorov and K. V. Belyaeva, *J. Chromatogr.*, 291 (1984) 416.
- 11 V. V. Bazyl'chick and P. I. Fedorov, *J. Anal. Chem. U.S.S.R.*, 38 (1983) 356.
- 12 E. A. Mistryukov, L. S. Savichev and V. V. Gavrilov, *Czechoslovak Chem. Soc. Chromatogr. Groups. Progress Chromatography (2nd Danube Sympos.)*, Carlsbad, Czechoslovakia, 1979, p. 18.
- 13 E. L. Tekova and E. A. Mistryukov, *Chromatographia*, 4 (1971) 77.

- 14 R. V. Golovnya, E. A. Mistryukov, S. K. Lesina and E. L. Gurchenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 7 (1977) 1632.
- 15 M. S. Vydergauz, A. A. Martynov and A. L. Samusenko, *Chemistry and Technology of Fuels and Oils*, Nauka, Moscow, 1972, pp. 10 and 55.
- 16 I. I. Bardyshev, R. I. Zen'ko, E. N. Manukov, G. I. Vojtechovskaya, K. A. Michalkovich and A. L. Perzovski, *Khim. Prir. Soedin*, 3 (1974) 3187.
- 17 I. I. Bardsyshev, R. I. Zen'ko, A. L. Perzovski and E. N. Manuskov, *Vestsi Akad. Navuk BSSR, Ser. Khim. Nauk.*, 2 (1975) 107.
- 18 V. V. Bazyl'chick, P. I. Fedorov and N. P. Polyakova, *All Union Conference on Utilization of Wood Extractives, Summaries of Reports, Gorki*, Gorki, 1982, p. 31.
- 19 V. V. Bazyl'chick, V. S. Shavyrin, V. N. Gusakov and N. P. Polyakova, *Zh. Obshch. Khim.*, 48 (1975) 582.
- 20 V. V. Bazyl'chick, V. S. Shavyrin, V. N. Gusakov, N. P. Polyakova, L. I. Shvarzbud and V. U. Erman, *Gydroliznaya e Lesokhimicheskaya Promyshlennost*, 2 (1976) 14.