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The Chemistry of the Natural Order Cupressales

XXXVII. * Monoterpenes from the Bark of *Juniperus communis* L.

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The monoterpene fraction of the essential oil from the bark of the common juniper has been investigated.

The steam volatile oil from the bark of the common juniper was first investigated by Hellström [1] and this work was reported by Mattson [2] in 1913. Two sesquiterpenes, juniperene and juniperol, were isolated. As the result of a recent reinvestigation [3] of the sesquiterpene fraction it was shown that juniperene is identical with kuromatsuene and with longifolene and that juniperol is identical with kuromatsuol and with the longiborneol obtained from longifolene by Naffa and Ourisson. The identity of juniperol and macrocarpol had been demonstrated earlier [4].

Mattson also reported the occurrence of *l*-α-pinene and sylvestrene (Δ^3-carene) in this essential oil. They were characterised as their hydrochlorides. Evidence was also obtained for the presence of camphene, phellandrene and dipentene.

We have now examined a low-boiling, neutral fraction of the essential oil from the bark of *Juniperus communis* and found it to contain about 30 % longifolene. 16 % consisted of a higher boiling sesquiterpene mixture. The monoterpene fractions were subjected to a gas chromatographic investigation [5] and the following monoterpenes were detected (approximate yields in parenthesis): α-pinene (22), Δ^3-carene (14), terpinolene (2), *cis*-menthane (1), β-pinene (1), limonene (1), myrcene (1), camphene (0.5), α-terpinene (0.5), γ-terpinene (0.5), β-phellandrene (0.5) and cymene (0.5 %).

It is interesting to note that Hendrickson [6] recently suggested that longifolene is derived from *cis*-farnesol. The same seems to apply to the sesquiterpenes hitherto isolated from the wood of several *Juniperus* species investigated in this laboratory by Runeberg [7] and by Bredenberg [8], *e.g.* cadinenes, cedrene, cuparene and thujopsene [9].

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Šorm *et al.*[10] investigated the berry oil of *Juniperus communis* in considerable detail and found sesquiterpenes derivable both from *cis*- and *trans*-farnesol (*e.g.* cadinane and selinane derivatives). Bark and wood are relatively simple organs contrary to the berries that consist of the united, fleshy cone scales and the seeds. A separate investigation of the two components of the berries would therefore seem to be a matter of interest. Apart from *J. sabiniana* little is known about the composition of the needle oils of junipers. In most cases commercial oils from conifer "needles" include volatile constituents of the twigs. For taxonomic purposes it is important that the constituents of as simple organs as possible are compared[11]. Results from investigations of complex organs or products from non-homogeneous starting materials must be used with care.

EXPERIMENTAL

The neutral part of the steam volatile oil from juniper bark was subjected to a preliminary rough vacuum-distillation to remove the highest boiling products. The fraction b.p. <120°/3 mm (A) was then fractionally distilled using a vacuum jacketed, packed column (LKB). The results are given in Table 1.

Table 1. Fractional distillation of the essential oil from the bark of *J. communis*.

Fraction	b.p./mm	Colour	n_D		$[\alpha]_D$	Yield (%)
I	64–70/33	Colourless	n_D^{21}	1.4670	−49.7°	22.7
II	70–74.5/33	»	n_D^{21}	1.4729	+9.63°	17.7
III	98–108/7	Slightly yellow	n_D^{21}	1.4892	−2.62°	4.4
IV	108–110/7	Slightly yellow	n_D^{22}	1.5031	+37.1°	25.5
V	110/7	Colourless	n_D^{23}	1.5033	+36.9°	4.5
VI	110–114/7	Very slightly yellow	n_D^{20}	1.5051	+13.5°	10.0
VII	107–110/3	Slightly yellow	n_D^{20}	1.5082	+4.16°	2.3
VIII	110–112/3	Yellow	n_D^{20}	1.5150	+10.02°	4.2
IX	Residue	Dark orange		—	—	8.9
						100.2

Fractions IV and V were almost pure longifolene (juniperene). Fractions I, II, and III were analysed by gas chromatography. A Perkin-Elmer Vapor Fractometer Model 154 in conjunction with a Speedmax Type G recorder (Leeds, Northrup Co) was used. The aluminium column was 4 m long and had an internal diameter of 5 mm. The stationary

Table 2. Constituents of fraction I.

Terpene	Relative retention volume	Yield (%)	% of A
α-Pinene	1.00	89.8	20.4
cis-Menthane	1.16	3.5	0.8
Camphene	1.24	1.7	0.4
β-Pinene	1.52	2.4	0.5
Δ^3-Carene	1.79	1.9	0.4
α-Terpinene	2.16	0.6	0.1
		99.9	22.6

phase was 60—80 mesh celite impregnated with 2,4-dinitrophenyl-2-naphthyl ether (m.p. 95°, 15 % by weight). The temperature was kept at 110° and the flow of helium 44 ml/min. The results are given in Tables 2, 3, and 4. In these tables the retention volumes of the various components are given in relation to α-pinene = 1. The amounts of the components were determined by measuring the area of the peaks with a planimeter.

Table 3. Constituents of fraction II.

Terpene	Relative retention volume	Yield (%)	% of A
α-Pinene	1.00	6.9	1.2
cis-Menthane	1.16	0.8	0.15
Camphene	1.24	0.4	0.08
β-Pinene	1.53	3.3	0.6
Myrcene	1.69	4.2	0.7
Δ^3-Carene	1.80	75.8	13.4
α-Terpinene	2.16	1.4	0.25
Limonene	2.34	2.6	0.46
β-Phellandrene	2.64	1.1	0.2
γ-Terpinene	2.85	0.2	0.04
Terpinolene	3.28	0.5	0.09
p-Cymene	3.55	2.7	0.7
		99.9	17.9

Table 4. Constituents of fraction III.

Terpene	Relative retention volume	Yield (%)	% of A
Δ^3-Carene	1.80	10.2	0.45
α-Terpinene	2.21	1.3	0.05
Limonene	2.38	16.0	0.70
β-Phellandrene	2.66	8.9	0.4
γ-Terpinene	2.88	13.5	0.6
Terpinolene	3.42	50.0	2.2
p-Cymene	3.60	trace	trace
		99.9	4.4

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REFERENCES

1. *Cf.* Hellström, A. *Östra Nyland-Kotka Nyheter*, Febr. 5th and 8th 1955.
2. Mattson, G. *Bidrag till kännedom af Finlands natur och folk.* Utgifna av Finska Vetenskapssocieteten. H. 72. No. 1. Helsingfors 1913.
3. Akiyoshi, S., Erdtman, H. and Kubota, T. *Tetrahedron* **9** (1960) 237.
4. Erdtman, H. and Thomas, B. *Chem. and Ind. London* **1955** 384.

5. *Cf.* Groth, A. *Svensk Papperstidn.* **61** (1958) 311 and forthcoming publication.
6. Hendrickson, J. B. *Tetrahedron* **7** (1959) 82.
7. Runeberg, J. *Acta Chem. Scand.* **14** (1960) 1288 and earlier and forthcoming papers.
8. Bredenberg, J. B-son. *Acta Chem. Scand. In the press.*
9. *Not published.* Reported at the Third Organic Chemistry Conference on The Chemistry of Natural Products and Organic Reaction Mechanisms held at Natick, Mass., October 1959.
10. *Cf.* Herout, V. and Sýkora, V. *Tetrahedron* **4** (1958) 247; Motl, O., Herout, V. and Šorm, F. *Collection Czechoslov. Chem. Communs.* **22** (1957) 785; **23** (1958) 1293.
11. Erdtman, H. In Todd, A. *Perspectives in Organic Chemistry.* Interscience 1956, p. 453; *Experientia*, Suppl. II, **1955** 156.

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