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The Chemistry of the Natural Order Cupressales

XXXI *. Heartwood Constituents of *Juniperus phoenicea* L.

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The heartwood of *Juniperus phoenicea* contains thujopsene, cuparene, cedrol, widdrol, "Widdringtonia acid II", hinokiic acid, nootkatin, β-thujaplicin and carvacrol.

The phoenicean juniper is widely distributed throughout the Mediterranean region, growing in dry situations on rocky hills. In Algeria it ascends to an altitude of about 6 000 feet. It also occurs in the Canary Islands where it is reported to attain a great age and enormous size [1].

Little has been published on the wood oil of *J. phoenicea*. Umney and Bennett [2] analysed an oil consisting mainly of α-pinene and also containing cadinene and traces of aldehydes. Rodié [3] made a study of an oil obtained from berryless branches. He identified pinene, camphene, phellandrene and cadinene and observed the presence of alcohols, esters and small amounts of aldehydes.

Commercial savin oil, obtained by steam distillation of branches and leaves of *J. sabina* has been adulterated by similar preparations obtained from *J. phoenicea*. Manceau [4] however noticed that while only about 24 % of the former oil distils below 170—175°, 79 % of the oil of *J. phoenicea* distils below 180°. This observation has been used to detect adulteration of savin oil. The oil described in this paper, obtained exclusively from heartwood, contained only about 4 % of monoterpenes or compounds with similar boiling points.

The previous paper [5] in this series described some constituents of *Juniperus cedrus*. This paper deals with the heartwood constituents of a sample of *J. phoenicea* obtained from the island of Cyprus.

The wood was extracted with acetone and the light petroleum-soluble part of the acetone extract was separated into neutral and acid fraction. Crystallisation of the acidic material gave "Widdringtonia acid II" [6], m.p. 190.0—191.5° and hinokiic acid [7]. The presence of nootkatin, β-thujaplicin and carvacrol in the remaining acidic material was shown by paper chromatography.

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The neutral oil was distilled. The lowest boiling part of the oil, which apparently contains monoterpenes, has not been investigated. The next higher boiling sesquiterpene fraction had a relatively simple composition with thujopsene [7] as the main constituent.

J. phoenicea appears to be the most convenient source of thujopsene so far encountered. In all thujopsene-producing conifers so far investigated in this laboratory thujopsene occurs mixed with comparatively large amounts of compounds with very similar boiling points such as α-cedrene or certain incompletely characterised dextrorotatory sesquiterpene hydrocarbons. Large amounts of pure thujopsene can, however, be obtained by a simple distillation of the oil described in this paper.

The highest boiling part of the sesquiterpene hydrocarbon fraction was ozonised at low temperature and the material unaffected by ozone was identified as cuparene [8].

One of the sesquiterpene alcohol fractions crystallised on standing. The crystalline part was separated by chromatography into cedrol and widdrol [6].

Carbonyl compounds present in the residue obtained on distillation of the neutral oil were isolated using the Girard D reagent.

The compounds isolated are listed below with very approximate estimates of the amounts present (as percentages of the air-dried wood). Total acetone extract 8.9, ether-soluble acetone extract 7.5, light petroleum-soluble acetone extract 6.0, sodium bicarbonate-soluble 0.03, potassium hydroxide-soluble 0.5, neutral 5.5, carvacrol 0.1, "Widdringtonia acid II" 0.1, hinokiic acid 0.04, thujopsene 2.2, cuparene 0.08, cedrol 0.2, widdrol 0.003, high-boiling carbonyl compounds 0.05.

EXPERIMENTAL

Rotations were measured in chloroform unless otherwise specified; melting points, taken on a hot stage, are corrected; boiling points are uncorrected. Light petroleum refers to the fraction b.p. 40–60°.

The air-dried heartwood of *J. phoenicea* (7.0 kg) was extracted with acetone for 24 h and fractionated as described in a previous paper in this series [11] (precipitate A, 96 g, precipitate B 108 g, sodium bicarbonate-soluble oil C 2.3 g, potassium hydroxide-soluble oil D, 35 g, neutral oil E, 384 g).

Alkali-soluble fraction. The oil D crystallised partly on standing. The crystals (F, 6.0 g) were filtered off and the remaining oil was dissolved in ether and separated into a sodium carbonate-soluble fraction (G, 15.1 g) and a sodium carbonate-insoluble oil (H, 11.5 g). A crude tropolone fraction (I, 1.22 g) was separated from this oil *via* the copper complexes.

A sample of fraction F was fractionated by crystallisation from ether. The material less soluble in ether was sublimed in a high vacuum, m.p. 190.0–192.0°, and identified (mixed m.p., I.R.) as the "acid II", isolated from *Widdringtonia* [6]. The material slightly more soluble in ether, m.p. 165.5–167.0°, was identified as *hinokiic acid* [7]. From fraction G an additional amount (2.1 g) of the above mixture of acids crystallised on standing.

On paper chromatography [9] fractions I and G were shown to contain *nootkatin* and *β-thujaplicin*. Paper chromatography also showed the presence of *carvacrol* in the oil H.

By a fast preliminary distillation the neutral oil E was divided into fraction K, b.p. up to 50°/70 mm (16.0 g), fraction L (264 g), b.p. 50°/70 mm–140°/1 mm, and a residue M (100 g). The oil L was distilled through a 1 m, vacuum-jacketed, packed column giving the fractions listed in Table 1.

Table 1. Distillation of neutral fraction L. Total distillate 220 g or 83 %.

Fraction	Weight (g)	B.p./15 mm Hg (°C)	Rotation $[\alpha]_D$	Refractive index (n^{25}_D)
Ia	13.7	123–127	−94	1.5020
Ib	21.2	127	−101	1.5026
Ic	26.5	127	−106	1.5030
Id	22.7	127	−109	1.5031
Ie	23.4	127	−115	1.5031
If	34.0	127–128	−106	1.5030
Ig	21.1	128–138	−12	1.5070
Ih	13.9	138–147	+ 52	1.5093
Ii	10.9	147–154	+ 34	1.5071
Ik	18.5	154–156	+ 37	—
Il	14.4	156–159	+ 25	1.5060

Gas chromatographic analysis of sesquiterpene hydrocarbon fractions. Gas chromatograms were run on a Pye Argon Chromatograph as described in a previous paper in this series [10]. (Temperature 150°, charge 0.025 μl.)

In Table 2 the approximate areas of individual peaks of different retention times are given as percentages of total peak area.

Identification of thujopsene. Fraction Ie (2.0 g) in ethanol (95 %, 40 ml) was refluxed with selenium dioxide (1.2 g) for 4 h and the product was filtered and evaporated to dryness. The crystalline residue (1.8 g) was recrystallised from light petroleum and sublimed in a high vacuum, m.p. 73.5–74.5°, and identified as widdrenal [6,7] (mixed m.p., I.R.).

Cuparene. Fraction Ih (3.0 g) was ozonised and treated as described in a previous paper [10]. The material unaffected by ozone (0.43 g), b.p. 121°/10 mm), $[\alpha]_D$ + 65° (*c*, 2.1), n_D^{25} 1.5200, was identified as cuparene [8] by comparing its physical constants and infrared spectrum with those of an authentic sample.

Sesquiterpene alcohols. Fraction Ik crystallised partly on standing. A sample (5.1 g) was mixed with ethanol (95 %, 10 ml), filtered and the crystalline precipitate (1.8 g) was chromatographed on basic alumina (40 g). Ether-benzene (1:99) eluted *cedrol* (1.60 g), recrystallised from ethanol (95 %), m.p. 85.0–86.0°, $[\alpha]_D$ + 11° (*c*, 1.7) and ether-benzene (1:1) eluted *widdrol* [6] (0.09 g), sublimed twice in a high vacuum, m.p. 95.0–96.0°, $[\alpha]_D$ + 103° (*c*, 2.2) (identifications by mixed m.p. and I.R.).

Table 2. Gas chromatographic analysis of the sesquiterpene hydrocarbon fractions in Table 1. Argon flow rate 25 ml/min.

Fraction	Peak retention time (min)				
	15.1	21.0	29.8	33.2	46.0
Ia	1	99			
Ib–If		100			
Ig		58	12	19	11
Ih			10	47	43

With an argon flow rate of 25 ml/min the retention times of the following known compounds were: thujopsene 21.0, and cuparene 46.0.

High-boiling carbonyl compounds. A liquid mixture of carbonyl compounds (N, 0.16 g) was separated from a sample of the neutral distillation residue M (5.0 g) using Girard D reagent (2.0 g) as described in a previous paper in this series [10].

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