

The Chemistry of the Natural Order Cupressales

XXVII*. Heartwood Constituents of *Juniperus utahensis* Lemm.

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From the heartwood of *Juniperus utahensis* there were isolated: thujopsene, cuparene, widdrol, "Widdringtonia diol", a yellow compound $C_{20}H_{20}O_5$, carvacrol, nootkatin, hinokiic acid as well as a hydroxy acid and a carbonyl containing compound, both probably of a sesquiterpene nature. The presence of β -thujaplicin was indicated by paper chromatography and that of α -cedrene by gas chromatography.

The available literature on juniper wood constituents deals mainly with the isolation and fractionation of essential oils and describes their physical constants. Only in a few cases have the various constituents present been identified. In a previous paper¹ in this series, however, an account was given of a more detailed chemical investigation of the Far Eastern species *Juniperus chinensis* in which a dozen of the heartwood constituents were identified. This paper deals with the constituents of the American desert juniper, *J. utahensis*.

The only previous investigation of this species that has been published was carried out by Adams and Billinghurst² who described an oil obtained by steam distillation of leaves and small twigs. They gave the physical constants of the oil but did not isolate or identify any of its constituents.

The wood used in the present investigation came from a tree grown at Grand Canyon, Arizona, U.S.A. It had been cut at least three years before it was worked up and was therefore rather dry.

The wood was extracted with acetone. The ether-soluble portion of the acetone extract was poured into a large volume of light petroleum giving a yellow crystalline precipitate.

On recrystallisation the compound melted with decomposition at 313° and analysed for $C_{20}H_{20}O_5$. The mass spectrum confirmed the molecular weight as 340. The compound contained no methoxyl group; the C-methyl determination gave 1.4 moles of acetic acid. The infrared spectrum (see Fig. 1) indicated

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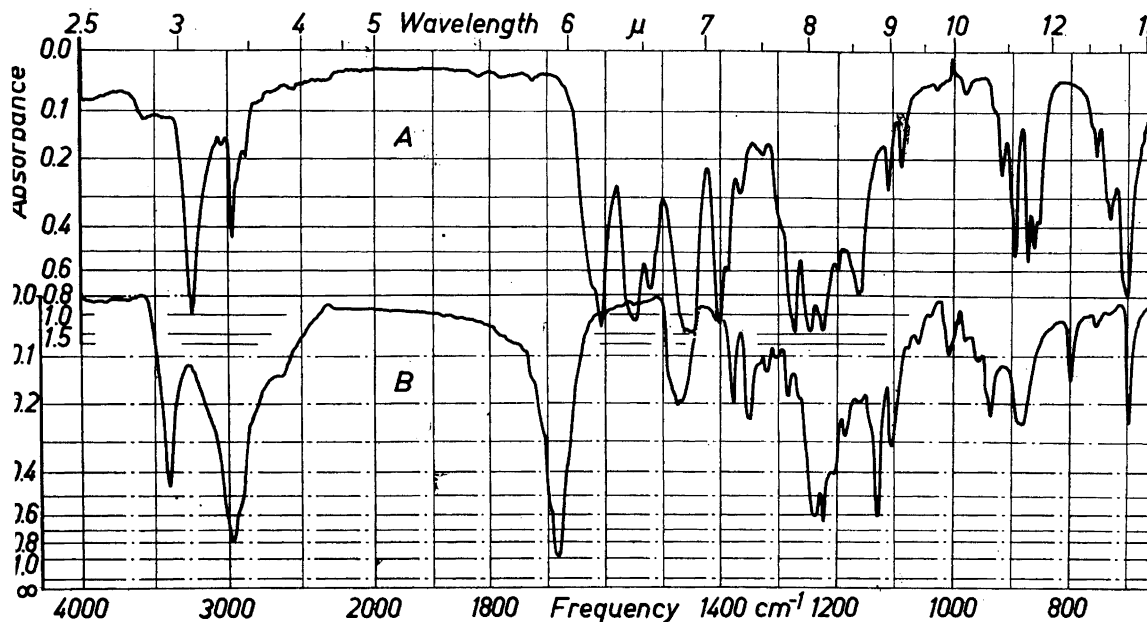


Fig. 1. Infrared spectra of utahin (A) and of hydroxy acid m. p. 181–187° (B) in potassium bromide.

the presence of at least one phenolic hydroxyl group ($3\ 250\text{ cm}^{-1}$). The absorption at $1\ 615\text{--}1\ 650\text{ cm}^{-1}$ and the broad, weak OH-absorption near $2\ 500\text{ cm}^{-1}$ may indicate the presence of a strongly hydrogen-bonded keto function in the molecule. The ultraviolet spectrum of the compound is given in Fig. 2.

Zinc dust distillation afforded a semi-solid product with ultraviolet absorption maxima at 245, 253 and 282 $m\mu$. Selenium dehydrogenation gave a very small yield of a product with maxima at 274 and 277 $m\mu$. Catalytic hydrogenation afforded only unidentifiable products. The compound gave a negative magnesium-hydrochloric acid test.

The name utahin is proposed for the above compound which to our knowledge has not previously been isolated.

Acetylation of utahin afforded a pale yellow di-acetate, $C_{24}H_{24}O_7$, m.p. 205° (decomp.), which was not found to be optically active. Its infrared spectrum showed no absorption band at $3\ 250\text{ cm}^{-1}$ but the absorption in the $1\ 615\text{--}1\ 650\text{ cm}^{-1}$ and $2\ 500\text{ cm}^{-1}$ regions was unchanged. The ultraviolet spectrum of utahin diacetate is given in Fig. 2.

Since the wood used in this investigation had been stored for several years it is possible that utahin may be an artefact formed by oxidation during storage. To check this possibility a large sample of fresh wood (grown near Ogden, Utah, U.S.A.) was obtained. This material also afforded utahin but in considerably lower yield (0.001 %, see below). It therefore seems likely that utahin

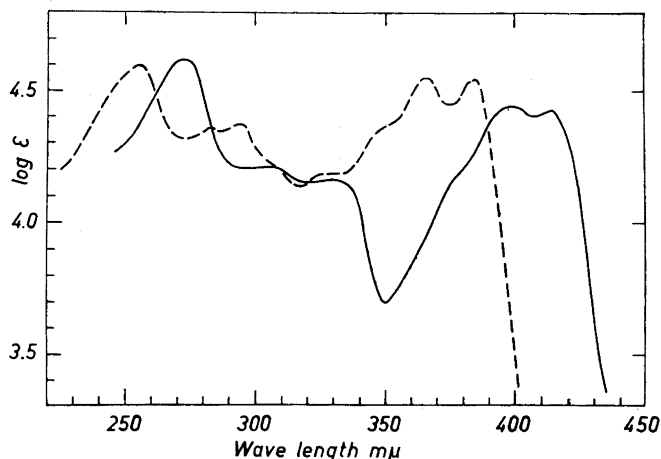


Fig. 2. Ultraviolet spectra of utahin (—) in chloroform and of utahin diacetate (-----) in ethanol (95 %).

is present in the fresh wood although the possibility that it may have been formed during working up cannot be excluded.

The diterpenes ferruginol, sugiol and xanthoperol have recently been isolated from *J. communis*³⁻⁵. The empirical formula and the C-methyl content of utahin suggest that it could be related to these diterpenes. Further work on utahin is in progress.

The light petroleum-soluble part of the acetone extract, on standing, gave a yellowish crystalline precipitate (C, see experimental part). The infrared spectrum of this material, except for additional carbonyl absorption (1745 cm^{-1}) showed great resemblance to that of utahin but it has not yet been investigated.

The remaining light petroleum-soluble acetone extract was separated into neutral and acid fractions by extraction with alkali. The acidic material afforded two sesquiterpene acids.

One of these was hinokiic acid⁶ which has also been found in *J. chinensis*¹ as well as in several other trees of the Cupressaceae.

The other acid was a new sesquiterpene hydroxy acid $\text{C}_{15}\text{H}_{24}\text{O}_3$, m.p. $181-187^\circ$; unchanged by further recrystallisation or sublimation. Since the acid could not be catalytically hydrogenated, the analysis suggests that the compound may be tricyclic. Except for a very weak maximum at $206\text{ m}\mu$ ($\epsilon = 63$), the ultraviolet spectrum showed no significant absorption in the $195-350\text{ m}\mu$ region.

Although the compound itself melted over a wide range, it gave a sharp-melting methyl ester (m.p. $98.0-98.5^\circ$) with diazomethane. The ester was reduced to a diol which was dehydrogenated with selenium giving a product that, according to the ultraviolet spectrum, was mainly benzenoid in nature. The dehydrogenation product was chromatographed on alumina but

none of the fractions gave a crystalline picrate. The hydroxy acid was stable to chromic acid in pyridine at room temperature indicating that the alcoholic hydroxyl group is tertiary. Dehydration with formic acid yielded a product which gave a satisfactory analysis but had no sharp melting point and was probably a mixture of isomers. The ultraviolet spectrum showed only a maximum at 205 $m\mu$ indicating that the product did not contain an α - β -unsaturated acid. Further work on the structure of this hydroxy acid is in progress.

The remaining acidic material from the light petroleum-soluble acetone extract gave carvacrol on distillation. The tropolones were concentrated by precipitation with copper acetate and decomposition of the crude copper salts with hydrochloric acid. Chromatography of the product obtained gave nootkatin and paper chromatography indicated the presence of β -thujaplicin.

The neutral oil was distilled. Fraction 1 (Table 1) corresponded to a wide boiling point range and according to its infrared spectrum appeared to be a complex mixture of carbonyl compounds, hydrocarbons and alcohols. Fraction 2 consisted almost entirely of hydrocarbons and fraction 3 again showed hydroxyl absorption. Gas chromatography of the first three fractions indicated the following compositions (in percent), assuming complete resolution: Fraction 1 (Table 1), thujopsene ⁶ 55; α -cedrene 31; two unknowns 7 and 7. Fraction 2, thujopsene 62; α -cedrene 13; four unknowns 10, 8, 6 and 1. Fraction 3, thujopsene 16; cuparene ⁷ 34; two unknowns 34 and 16.

The major component of fraction 2 (Table 1) was shown to be thujopsene by conversion to the corresponding aldehyde (widdrenal) ^{6,8}. Fraction 3 (Table 1) was ozonised at low temperature and the material unaffected by ozone was identified as cuparene.

The next higher boiling fraction gave widdrol ⁸ but no cedrol was detected. However since α -cedrene is present it is not improbable that cedrol might also occur in the wood although in very small amount. The same fraction, on ozonolysis followed by chromatography, afforded a sesquiterpene diol, m.p. 154°, previously isolated from *Widdringtonia juniperoides* ⁸.

Fraction 5 (Table 1) contained a crystalline carbonyl compound which is probably a sesquiterpene but gave a poor analysis.

The compounds isolated are listed below with very approximate estimates of the amounts present (as percentages of the air-dried wood). Total acetone extract 9.3, ether-soluble acetone extract 6.3, light petroleum-soluble acetone extract 1.8, sodium bicarbonate-soluble 0.084, sodium hydroxide-soluble 0.67, neutral 1.1, utahin 0.030, nootkatin 0.0002, β -thujaplicin 0.0001, carvacrol 0.0072, hinokiic acid 0.013, sesquiterpene hydroxy acid 0.070, α -cedrene 0.048, thujopsene 0.18, cuparene 0.047, widdrol 0.051, "Widdringtonia diol" m.p. 154°, 0.0003, high boiling carbonyl compounds 0.020.

EXPERIMENTAL

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

Isolation of the oils: The ground, air-dried heartwood (9.7 kg) was continuously extracted with acetone for 24 h. The acetone was evaporated and the remaining oil poured with stirring into ten volumes of ether. The ether solution was filtered (precipitate A, 312 g), evaporated and the residue was poured into ten volumes of light petroleum. After filtration (precipitate B, 437 g) the solution was evaporated almost to dryness. On standing for about one month a yellow crystalline precipitate formed (C, 0.373 g). This was removed by filtration. The filtrate was diluted with two volumes of light petroleum and extracted successively with a saturated solution of sodium bicarbonate and 2 N sodium hydroxide. On acidification and extraction with ether the sodium bicarbonate solution yielded a viscous oil (D, 8.1 g) which was not further investigated. The sodium hydroxide-soluble material (E, 65.3 g) was isolated in the same way by acidification and extraction with ether. The light petroleum solution was washed with water, dried and evaporated yielding neutral material (F, 104.0 g).

Precipitate B

Isolation of utahin. Precipitate B was dissolved in an equal amount of acetone. On standing a yellow precipitate (2.8 g) formed. It was separated by filtration, washed with acetone, recrystallised from a large volume of ethyl acetate and sublimed in a high vacuum, m.p. 313° (decomp.) (Found: C 70.6; H 6.2; CH_3O 0.1. $\text{C}_{20}\text{H}_{20}\text{O}_5$ requires C 70.6; H 5.9.) The melting point did not change on further recrystallisation and sublimation. (Found: C 70.9; H 6.0; O 23.3; $\text{CH}_3\text{-(C)}$ 6.2. $\text{C}_{20}\text{H}_{20}\text{O}_5$ requires O 23.5; $\text{CH}_3\text{-(C)}$ (one) 4.4.)

The mass-spectrum was recorded on an instrument with an all-glass, heated inlet system⁹. Only major peaks are given. The figures in brackets are intensities given as *per cent* of the strongest peak ($m/e = 43$). 340 (21), 312 (17), 284 (18), 270 (8), 269 (40), 253 (8), 128 (9), 127 (24), 115 (20), 105 (9), 91 (13), 77 (13), 69 (10), 67 (11), 63 (9), 57 (13), 55 (29), 53 (17), 51 (10), 45 (9), 44 (21), 42 (13), 41 (61), 39 (25), 29 (25), 28 (23), 27 (29), 18 (95), 17 (17) and 15 (10).

Utahin sublimed easily in a high vacuum and had a low solubility in most organic solvents except chloroform. It dissolved in concentrated sulphuric acid giving a pale greenish solution from which it could be recovered by addition of water. A solution in 95 % ethanol gave a brownish colour with aqueous iron (III) chloride. The compound does not dissolve in aqueous sodium hydroxide (2 N) but affords a bright orange salt with alkali. Utahin does not react with carbonyl reagents or with *o*-phenylene diamine in acetic acid.

Because of its very low solubility in ether, utahin was expected also to occur in the precipitate A. This was therefore extracted with chloroform, the extract was evaporated and the residue was dissolved in acetone (50 ml). Only a small amount of utahin (130 mg) precipitated on standing.

The wood remaining after acetone extraction was dried and extracted exhaustively with chloroform. Only a very small amount of utahin was obtained from the chloroform extract.

Utahin diacetate. Utahin (70 mg) in acetic anhydride (2 ml) was treated with perchloric acid (1 drop), the mixture was heated on a boiling water bath for 1 h and poured on to ice. The pale yellow crystalline material formed was separated and recrystallised from 95 % ethanol, m. p. 207° (decomp.), $[\alpha]_D$ 0. (Found: C 68.0; H 5.6; $\text{CH}_3\text{-CO-}$ 19.7. $\text{C}_{24}\text{H}_{24}\text{O}_7$ requires C 67.9; H 5.7; $\text{CH}_3\text{-CO-}$ (one) 10.6.)

Alkali-soluble fraction

Hinokiic acid. The alkali-soluble oil E on standing deposited a crystalline material (1.23 g). This was filtered off and recrystallised from light petroleum, m. p. 166.0–167.5° $[\alpha]_D -87^\circ$ (*c* 1.6). It was identified as hinokiic acid⁶ (mixed m. p., I.R.).

Hydroxy acid. The material remaining after separation of hinokiic acid from the oil E was dissolved in ether and extracted with aqueous sodium carbonate (2 N). The ether solution on evaporation gave an oil (G). The sodium carbonate solution on acidification and extraction with ether gave a product (36.4 g) which was mixed with light petroleum

and partly crystallised on standing for several months. The crystals (6.76 g) were separated by filtration (filtrate, oil [H]), recrystallised several times from ligroin (b. p. 100–125°) and from ethanol-water and were then sublimed in a high vacuum, m. p. 181–187°, $[\alpha]_D -47^\circ$ (c, 3.2). (Found: C 71.9; H 9.7; M (Rast) 250; M (titr.) 207; $\text{CH}_3-(\text{C})$ 7.4. $\text{C}_{15}\text{H}_{24}\text{O}_2$ requires C 71.4; H 9.6; M 252; $\text{CH}_3-(\text{C})$ (one) 6.0.) Further recrystallisation from these solvents and sublimation did not change the melting point (181–187°), (C 71.1; H 9.2).

Hydroxy acid methyl ester. The hydroxy acid (400 mg) was methylated with diazomethane. The ester was recrystallised from ethanol-water and sublimed in a high vacuum, m. p. 98.0–98.5, $[\alpha]_D -25^\circ$ (c, 1.0). (Found: C 72.1; H 9.5; M (Rast) 252. $\text{C}_{15}\text{H}_{24}\text{O}_2$ requires C 72.1; H 9.8; M 266.)

Diol. A solution of the hydroxy acid methyl ester (595 mg) in absolute ether was added dropwise with stirring at 0° to a solution of lithium aluminium hydride (455 mg) in absolute ether. After 3 h at room temperature the excess reagent was destroyed with ethyl acetate. Hydrochloric acid (2 N) was added and the solution was extracted with ether. On evaporation the ether solution afforded a substance (518 mg) which was recrystallised from cyclohexane and sublimed in a high vacuum, m. p. 130.0–131.0°, $[\alpha]_D +6^\circ$ (c, 2.0). (Found: C 75.4; H 10.9. $\text{C}_{15}\text{H}_{24}\text{O}_2$ requires C 75.6; H 11.0.)

Attempts to hydrogenate the hydroxy acid. Hydroxy acid (60 mg) in 95 % ethanol (10 ml) or in acetic acid was shaken with a platinum oxide catalyst (6 mg) in a hydrogen atmosphere for 6 h. No hydrogen was absorbed and the starting material was recovered unchanged.

Attempted oxidation with chromic acid. Hydroxy acid (21 mg) was added to a solution of chromic acid (32 mg) in glacial acetic acid (2 ml) and dry pyridine (1 drop). After 15 h at room temperature methanol (0.3 ml) was added and the mixture left to stand for another 15 h. It was then acidified with sulfuric acid (2 N) and extracted with ether; the ether solution was washed with water, dried and evaporated. The residue, after recrystallisation from ethanol, afforded unchanged starting material.

Dehydration of the hydroxy acid. A mixture of the hydroxy acid (355 mg) and formic acid (90 %, 7 ml) was heated on a water bath for 2 h. Ether was added and the solution was extracted with aqueous sodium bicarbonate. The ether solution was evaporated affording a residue which was recrystallised from 95 % ethanol and sublimed in a high vacuum, m. p. 87–93°. (Found: C 77.1; H 9.2; $\text{CH}_3-(\text{C})$ 11.7. $\text{C}_{15}\text{H}_{22}\text{O}_2$ requires C 76.9; H 9.5; $\text{CH}_3-(\text{C})$ (one) 6.4.)

Carvacrol. A sample (17.8 g) of the sodium carbonate insoluble oil (G) was distilled through a spinning band column. The material distilled over a range of 108–170°/20 mm without giving any definite fraction of constant boiling point. The material boiling at 113–122°/20 mm was mainly carvacrol. This fraction was converted into carvacroxy acetic acid, m. p. 151–152°, undepressed by an authentic sample.

The sodium carbonate insoluble oil (G, 10.0 g) was dissolved in ligroin (b.p. 100–125°) and shaken with aqueous copper acetate (saturated). The liquid phases were removed by filtration and the copper salts remaining were washed with ligroin and water, decomposed with hydrochloric acid (2 N) and the product was extracted with ether. On evaporation of the ether solution a viscous oil (I, 481 mg) was obtained. This was chromatographed on silica gel. The silica gel was made iron-free by treatment with aqueous oxalic acid (saturated) and washing with water. It was then treated with a solution of the disodium salt of ethylene diamine tetra-acetic acid (0.002 M), washed with water and dried. The isopropyl ether-soluble part of the oil I (232 mg) was chromatographed on this pretreated silica gel (40 g) using isopropyl ether as eluent. 200 ml fractions were collected. Each fraction was evaporated and analysed by paper chromatography¹⁰. Fraction 1 consisted mainly of a yellow compound which was not further investigated, fraction 2 of a mixture of this compound and nootkatin, fraction 3 of nootkatin and a small amount of β -thujaplicin. The crystalline part of this fraction (4 mg) was recrystallised from light petroleum, m. p. 96.0, and identified as *nootkatin* (mixed m. p., I.R.). Fraction 4 consisted of β -thujaplicin, nootkatin and three further compounds with lower R_F values than the first two, fraction 5 mainly of β -thujaplicin which however could not be crystallised.

Neutral fraction

The neutral oil F was fractionally distilled through a one metre, vacuum-jacketed, packed column, giving the fractions listed in Table 1.

Table 1. Distillation of fraction F. Total distillate 81.7 g or 80 %.

Fraction	Weight (g)	B.p. (°C)	Pressure (mm Hg)	Rotation ([α] _D)	Refractive index (n_D^{25})
1	11.3	101.0–126.5	14	–44.4	1.4933
2	14.9	126.5–135.0	14	–66.4	1.5040
3	12.8	135.0–155.5	14	+27.4	1.5094
4	12.0	155.5–156.0	14	+42.9	1.5079
5	17.8	156.0–160.5	14	+12.6	1.5117
6	12.9	up to 230°	2	+ 3.9	1.5202

Gas chromatographic examination of the sesquiterpene hydrocarbon fractions. A Pye Argon Chromatograph, Cat. No. 12 000, was used together with a Philips Automatic Compensator PR 2210 A/21. (Column length 1.20 m, internal column diameter 5 mm, stationary phase 100–115 mesh Silocel C 22 brick powder impregnated with 2,4-dinitrophenyl-2-naphthyl ether (15 %) and dibenzylpyridine (a mixture of 2,4- and 2,6-isomers, 0.75 %) ¹¹, temperature 150°, charge 0.025 μ l, argon flow rate 0.32 ml/sec.

The following peaks were obtained. Recorder deflection (mV) given as a function of time (min). Fractions refer to those in Table 1.

Fraction 1, 9 (17.8); 23 (24.9); 60 (27.2); 9 (29.6).

Fraction 2, 2 (17.8); 12 (24.9); 66 (27.2); 4 (34.7); 4 (39.2); 5 (42.7).

Fraction 3, 7 (27.2); 11 (42.4); 9 (48.9); 8 (60.0).

The peak at 24.9 min corresponded to synthetic *a-cedrene* prepared from cedrol, the peak at 27.2 min to pure thujopsene and the peak at 60.0 min to cuparene.

Thujopsene. Fraction 2 (Table 1, 2.1 g) in 95 % ethanol (40 ml) was refluxed with selenium dioxide (1.2 g) for 4 h. The product was filtered, evaporated to dryness and the residue distilled in a high vacuum. On standing a crystalline precipitate (372 mg) was formed; this was collected by filtration, recrystallised from light petroleum, m. p. 73.5–74.5° and identified as widdrol ⁸, (mixed m. p., I.R.).

Cuparene. Fraction 3 (Table 1) was redistilled through a spinning band column. The fraction (1.36 g) showing the strongest absorption at 1 525 cm^{-1} was ozonised in methylene chloride at –70°C until an excess of ozone was indicated by the appearance of a blue colour. When the reaction mixture had reached room temperature, hydrogen peroxide (30 %, 4 ml) in potassium hydroxide (10 %, 1.5 ml) was added dropwise. A large quantity of ether was added, the organic phase was separated, washed with water and evaporated giving a viscous oil. This was chromatographed on basic alumina (40 g). The first 100 ml of light petroleum eluted a hydrocarbon (191 mg) which was distilled under reduced pressure. The fraction boiling at 115°/7 mm, n_D^{25} 1.5215, [α]_D +65° (c, 1.9) was identified with *cuparene* ⁷ by comparing its physical constants and infrared spectrum with those of an authentic sample.

Widdrol. Fraction 4 (Table 1) crystallised partly on standing. A sample of this fraction (7.0 g) was filtered, the crystals (684 mg) were washed with light petroleum and recrystallised from acetonitrile, m. p. 95.0–96.0°, [α]_D +103° (c, 2.1) identified as widdrol ⁸ (mixed m. p., I.R.).

Attempts to isolate cedrol. Crude widdrol obtained from fraction 4 (Table 1, 204 mg) was chromatographed on basic alumina. Light petroleum eluted a small quantity of hydrocarbon; 2 % ether in benzene gave an oil with an infrared spectrum different from that of cedrol; ether-benzene (1:1) eluted widdrol.

A sample (1.52 g) of the mother liquor obtained when widdrol was separated from fraction 4 (Table 1) was ozonised as described for cuparene (see above) and the product separated into acidic and neutral fractions with sodium carbonate (2 N). The neutral fraction was chromatographed on basic alumina but no cedrol could be detected. Crude widdrol (204 mg) obtained from fraction 4 (Table 1) was ozonised and chromatographed in the same way but no cedrol was obtained in this case either.

"*Widdringtonia diol*." In the chromatography of the neutral part of the ozonisation product obtained from crude widdrol, elution of the column with methanol gave a crystalline compound (4 mg). This was recrystallised from light petroleum, m. p. 153–154° and identified (mixed m. p., I.R.) as a "diol" previously isolated from *Widdringtonia juniperoides*⁸.

High boiling carbonyl compounds. A sample of fraction 5 (Table 1, 10.0 g) in 95 % ethanol containing 10 % acetic acid (30 ml) was refluxed with Girard D reagent (3.0 g) for 30 min. The reaction mixture was diluted with about five volumes of ice-water and extracted with ether. The aqueous phase was acidified with an equal volume of hydrochloric acid (4 N) and extracted with ether. The ether solution, on evaporation, afforded an oil (1.09 g) which partly crystallised on standing. The crystals (183 mg) were separated by filtration, washed with light petroleum, recrystallised from the same solvent and sublimed in a high vacuum, m. p. 107.5–108.0°, $[\alpha]_D +75$ (c, 1.4). (Found: C 81.5, 81.1; H 10.5, 10.2; $C_{15}H_{14}O$ requires C 81.8; H 11.0.) 2,4-dinitrophenyl-hydrazone, m. p. 198–199°.

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