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STUDIES ON THE ESSENTIAL OIL OF *CYPERUS ARTICULATUS* L.

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Abstract—The essential oil of *Cyperus articulatus* L. has been found to contain myrtenal, myrtenol, copaene, an unidentified hydrocarbon isomeric with copaene, a new sesquiterpenoid ketone articulone, and the corresponding alcohol articulol. Structures have been advanced for the last two.

Cyperus articulatus L. is a tropical sedge widely distributed in West Africa, where its rhizomes are used as a fumigant and perfume. Some preliminary investigations on the extraction of an essential oil from the rhizomes have been described.[1]

Although steam distillation has been reported unsatisfactory for extraction of the essential oil[1] we have used this procedure, and obtained the oil in about 1% yield from the dried plant material. The crude oil was distilled *in vacuo* to separate a small amount of involatile, tarry material. Its physical constants agreed reasonably well with those of the oil obtained by Joly[1] by extraction with benzene. The IR spectrum showed that the oil contained unsaturated species, alcohols and carbonyl compounds.

Careful fractionation of the oil *in vacuo* gave firstly a fraction b.p. 94–130°/10 mm, which was separated by chromatography into three sub-fractions: a *sesquiterpene hydrocarbon fraction*, a *monoterpene carbonyl fraction* and a *monoterpene alcohol fraction*. A higher-boiling fraction, b.p. 122–176°/5 mm, was similarly separated by chromatography into a *sesquiterpene carbonyl fraction* and a *sesquiterpene alcohol fraction*.

Sesquiterpene hydrocarbon fraction

Purification of the fraction by rechromatography and redistillation afforded a colourless oil, analysis of which supported a molecular formula $C_{15}H_{24}$. Gas chromatography showed that two sesquiterpene hydrocarbons were present, but although the separation was reasonably satisfactory on a 0·1 μl. scale, attempts to scale up were unsuccessful because of a deterioration in the resolution. Mass spectrometry of the two hydrocarbons was, however, possible, and showed that both had mol. wt 204 and were therefore both $C_{15}H_{24}$. Measurements of the areas enclosed by the peaks on the gas chromatogram showed the hydrocarbons were present in the ratio of about 55:45, though this ratio varied with different batches of essential oil.

Spectral measurements [λ_{max}^{MeOH} 204 mμ (ε 6000), ν_{max} 1631 and 787 cm^{-1}] showed that the fraction was unsaturated, and this was confirmed by its chemical reactions. IR absorption at 1383, 1370, 1175 and 1140 cm^{-1} was consistent with the presence of

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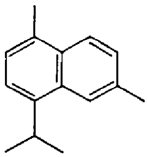
[1] L. Joly, *Parfumerie Moderne* 31, 25 (1937).

a CMe_2 group. Near IR absorption at 1·642 μ was very weak, and suggested that a cyclopropane methylene group was absent.[2]

Dehydrogenation of the fraction proceeded smoothly to give cadalene (I) in 80 % yield, which suggested that both hydrocarbons in the fraction were cadalene-type sesquiterpenes. Catalytic reduction in ethanol ceased when the uptake amounted to one mole of hydrogen. The product was a mixture of two saturated hydrocarbons,



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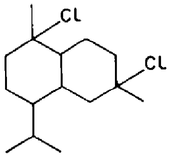

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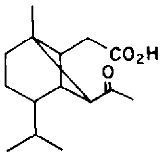

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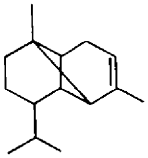


IV

$C_{15}H_{26}$, which were separable on a small scale by gas chromatography. The original hydrocarbons, therefore, are both tricyclic. Reduction in acetic acid, on the other hand, was more rapid and also ceased after uptake of one mole hydrogen, but the product showed four peaks when subjected to gas chromatography, possibly owing to differences in the stereochemical course of the two reductions.

Treatment of the hydrocarbon mixture with dry hydrogen chloride afforded cadinene dihydrochloride (II) in poor yield. Oxidation of the mixture with potassium permanganate yielded copaene ketonic acid (III), identified as its semicarbazone by comparison with an authentic specimen.[3,4] Evidently one of the components of the mixture is copaene (IV),[5,6] and this was confirmed by gas chromatographic comparison with an authentic sample. Copaene coincided with the first peak in the gas chromatogram. It has not so far been possible to separate and investigate the second hydrocarbon.

Monoterpene carbonyl fraction

The fraction was purified by re-chromatography and repeated fractional distillation *in vacuo*. Gas chromatography showed that the fraction was essentially homogenous. Analysis supported a molecular formula $C_{10}H_{14}O$, and IR measurements (strong bands at 2703, 1661 and 1608 cm^{-1}) suggested the presence of an αβ-unsaturated aldehyde, though the C=O band appeared at an abnormally low wave number. Chemical tests confirmed the aldehydic nature of the product. The UV absorption (λ_{max}^{MeOH} 243 mμ, ε 8000) confirmed the αβ-unsaturated aldehyde group, the abnormally long wavelength being explained by the inclusion of the chromophore in a strained, possibly bridged bicyclic, ring system.[7] Catalytic hydrogenation afforded a saturated dihydro-aldehyde, $C_{10}H_{16}O$, which must be bicyclic. A survey of the literature relating to bicyclic monoterpene αβ-unsaturated aldehydes suggested that the compound

[2] W. H. Washburn and M. J. Mahoney, *J. Amer. Chem. Soc.* **80**, 504 (1958); P. G. Gassman, *Chem. & Ind.* 740 (1962).

[3] F. W. Semmler and H. Stenzel, *Ber. Dtsch. Chem. Ges.* **47**, 2555 (1914).

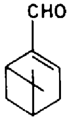
[4] L. H. Briggs and M. D. Sutherland, *J. Org. Chem.* **13**, 1 (1948).

[5] G. Büchi, S. H. Feairheller, P. de Mayo and R. E. Williams, *Proc. Chem. Soc.* 214 (1963).

[6] V. H. Kapadia, B. A. Nagasampagi, V. G. Naik and S. Dev, *Tetrahedron Letters* 1933 (1963).

[7] R. N. Moore and G. S. Fisher, *J. Amer. Chem. Soc.* **78**, 4362 (1956).

might be (—)-myrtenal (V), and an IR comparison between it and a sample of (+)-myrtenal prepared by oxidation of (+)-α-pinene showed that this was indeed the case. Both 2,4-dinitrophenylhydrazones had m.p. 222° and identical IR curves.



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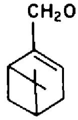

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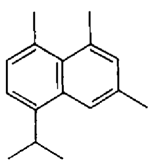

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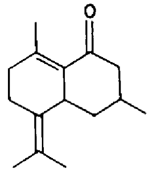

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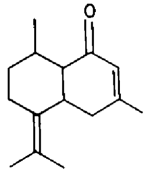

IX

Monoterpene alcohol fraction

Purification by repeated vacuum fractionation gave a product shown by gas chromatography to be virtually a single species. IR absorption showed the presence of OH, CMe_2 and $R^1R^2C{=}CHR^3$ functions, and the UV spectrum ($\lambda_{\max}^{\text{MeOH}}$ 209 mμ, ε 8800) was consistent with the presence of a single ethylenic chromophore, possibly an allyl alcohol group.[8] The presence of such a group was confirmed by oxidation with activated manganese dioxide[9] to (—)-myrtenal, which indicated that the alcohol was (—)-myrtenol (VI). Confirmation was effected by comparison of the alcohol with a specimen of (+)-myrtenol obtained by oxidation of (+)-α-pinene; the IR spectra of the alcohols and their *p*-nitrobenzoates were identical.

Sesquiterpene carbonyl fraction

Gas chromatography of the carefully purified fraction showed that it contained mainly one species, with two minor impurities. The product was converted to its 2,4-dinitrophenylhydrazone, m.p. 231-232°, which proved to be identical with the 2,4-dinitrophenylhydrazone of a sesquiterpene ketone isolated by Naves and Ardizio[10] from the essential oil of *Cyperus scarosius*. Hydrolytic cleavage[11] of the derivative afforded a ketone $C_{15}H_{22}O$, $\lambda_{\max}^{\text{MeOH}}$ 206 (ε 5350) and 250 mμ (ε 10,500), $\nu_{\max}$ 1678, 1634, 1387, 1376, 1181, 1166 and 890 cm^{-1}. It was concluded that the ketone, which we have called articulone, was αβ-unsaturated, and contained an additional isolated double bond and a CMe_2 group. The ratio of the integrated band intensities corresponding to the C=O and conjugated C=C groups was 6·5, indicating that the enone system was *transoid*.[12] Catalytic hydrogenation yielded firstly dihydroarticulone, $C_{15}H_{24}O$, which was not αβ-unsaturated but still contained an ethylenic bond, and ultimately tetrahydroarticulone, $C_{15}H_{26}O$, a saturated ketone, $\nu_{\max}$ 1715 $cm.^{-1}$ Articulone is therefore bicyclic, and the carbonyl group may be part of a six-membered ring.

Reduction of articulone with lithium aluminium hydride afforded the corresponding alcohol, articulol, as a mixture of isomers. Heating articulol with 30% palladized

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[8] Cf. F. Bader, *Helv. Chim. Acta* **34**, 1632 (1951); P. S. Ellington and G. D. Meakins, *J. Chem. Soc.* 697 (1960).

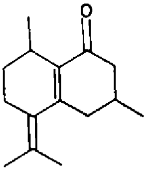
[9] O. Mancera, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.* 2189 (1953).

[10] Y.-R. Naves and P. Ardizio, *Bull. Soc. Chim. Fr.* 332 (1954).

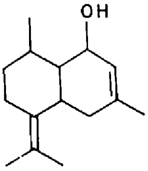
[11] J. Demaeker and R. H. Martin, *Nature, Lond.* **173**, 266 (1954).

[12] R. L. Erskine and E. S. Waight, *J. Chem. Soc.* 3425 (1960).

carbon at 300° caused dehydration and dehydrogenation to cadalene (I) in high yield. On the assumption that molecular rearrangement had not occurred, articulone is evidently a cadalene-type sesquiterpene. The position of the keto-group was settled by reaction of articulone with magnesium methyl iodide, to yield the tertiary alcohol methylarticulol, as a mixture of epimerides. Dehydration and dehydrogenation of this product gave 8-methylcadalene (VII). Since ozonolysis of dihydroarticulone afforded acetone in good yield, it would appear that articulone can be formulated as VIII or IX. The maximal UV absorption at 250 mμ favours, when Woodward's rules are applied,[13] structure VIII ($\lambda_{max}^{calc.}$ 254 mμ) and rules out the conjugated dienone X, though the IR spectrum (see above) favours the *transoid* enone system present in IX. A decision between VIII and IX was reached unequivocally by a study of the NMR spectrum of articulone. Spin decoupling shows the presence of the grouping $CH_3—\overset{|}{C}=\overset{|}{C}H$, with a conjugated vinyl proton signal at τ 4·40, and an allylic methyl proton signal at τ 8·02, tetramethylsilane being used as internal reference. This is in agreement with structure IX for articulone, and rules out the alternative VIII, which has no vinyl proton. Since IX is an α-octalone, it is presumed that the ring junction is the more stable *trans*.



X



XI

Sesquiterpene alcohol fraction

Gas chromatography of the re-chromatographed and redistilled fraction showed the presence of two major sesquiterpene alcoholic components, and three minor constituents. Oxidation with activated manganese dioxide afforded, after purification by chromatography, articulone (IX), identified as its 2,4-dinitrophenylhydrazone. One of the alcoholic components is therefore articulol, XI. Careful elution of the manganese dioxide oxidation mixture gave an unoxidized alcohol mixture containing on gas chromatographic evidence, one major and three minor components, which have not so far been successfully separated.

EXPERIMENTAL

Optical rotations were measured in $CHCl_3$. Gas chromatography was effected using a Pye Argon Chromatograph.

Extraction of the oil

The air-dried rhizomes (250 g), obtained from Nigeria, were steam distilled until the distillate was no longer turbid. The distillate was saturated with NaCl and subjected to continuous ether extraction for several hr. The dried, ethereal extract was concentrated and the residue distilled *in vacuo*, b.p. 86–177°/5 mm (2·50 g; 1% w/w of dried rhizomes), $d_4^{20°}$ 0·9849, $n_D^{20°}$ 1·5025,

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[13] R. B. Woodward, *J. Amer. Chem. Soc.* 63, 1123 (1941); 64, 76 (1942).

$[\alpha]_D^{20}$ −15·5° (*c*, 4·13). IR spectrum (liquid film): bands at 3600 (OH), 2732w (aldehyde C—H?), 1706 (saturated ketone carbonyl), 1678 (αβ-unsaturated ketone carbonyl), 1623 (conjugated C=C), 1381, 1370, and 1174 (CMe_2), 890 ($R^1R^2C{=}CH_2$), and 786 cm^{-1} ($R^1R^2C{=}CHR^3$).

Fractional distillation

The above oil (200 g) was distilled fractionally through a 15 cm column packed with ⅛″ × ⅛″ Dixon gauze rings, leading in the first instance to a low-boiling fraction b.p. 94–130°/10 mm (60 g), n_D^{20} 1·4973, $[\alpha]_D^{20}$ −14·5° (*c*, 3·10). This fraction (20 g), in light petroleum (b.p. 40–60°; 500 cc), was chromatographed on alumina (300 g). The column was eluted first with light petroleum (b.p. 40–60°; 2 l.), evaporation yielding a *sesquiterpene hydrocarbon fraction* (12·2 g). Elution with light petroleum (b.p. 40–60°)–benzene (1:1) afforded, after evaporation, a *monoterpene carbonyl fraction* (1·25 g), and a final elution with benzene–ethanol (5:1) gave a *monoterpene alcohol fraction* (4·65 g) after evaporation.

Sesquiterpene hydrocarbon fraction

Repeated fractionation *in vacuo* of the sesquiterpene hydrocarbon fraction afforded a colourless, mobile liquid, b.p. 72–73°/1·0 mm, 77–78°/2·5 mm, n_D^{15} 1·5069, $[\alpha]_D^{20}$ −10·9° (*c*, 2·01) [Found: C, 88·4, 88·3; H, 11·6, 11·65; M.W. (mass spectrometry), 204. $C_{15}H_{24}$ requires: C, 88·2; H, 11·8; M.W. 204]. A Kuhn–Roth estimation gave a value of 1·07 *C*-methyl groups. IR spectrum (liquid film): ν_{max} 1631 (C=C), 1383, 1370, 1175, 1140 (CMe_2), and 787 cm^{-1} ($R^1R^2C{=}CHR^3$). Near IR absorption: only very weak band at 1·642 μ (ε 0·06) (absence of cyclopropane methylene[14]). UV spectrum: λ_{max}^{MeOH} 204 mμ (ε 6000). The fraction decolourized cold $KMnO_4$ aq immediately, and gave an intense yellow colour with tetranitromethane. Gas chromatography using a 120 cm column of 20% polyethylene glycol adipate on 100–120 Celite at 100°, with an argon flow of 25 cc/min resolved the product into two sharp fractions with retention times of 40 and 47·5 min. Mass spectrometry of the separate fractions showed parent ion peaks of mass 204 in both spectra. The areas enclosed by the gas chromatography peaks were in the ratio of 55 (first peak) to 45. A 1:1 mixture of the hydrocarbon fraction and authentic copaene, subjected to gas chromatography under exactly the same conditions, gave the same two peaks as the former, but the area enclosed by the first peak was now about three times that enclosed by the second.

Dehydrogenation. The hydrocarbon fraction (2·27 g) and 30% Pd–C catalyst (0·25 g) were heated at 230° under N_2 for 5 hr. Addition of ether, filtration, evaporation and distillation yielded cadalene (1·84 g, 84%), b.p. 135–136°/5 mm. The picrate, prepared in ethanol, had m.p. 114–115° (Found: C, 58·9; H, 5·15; N, 9·6. Calc. for $C_{21}H_{21}N_3O_7$: C, 59·0; H, 4·95; N, 9·8%), alone or mixed with an authentic specimen of cadalene picrate (lit.[15] m.p. 114–115°). The X-ray powder photographs of the picrates were identical.

Catalytic hydrogenation. The sequiterpene hydrocarbon fraction (0·50 g) in ethanol (15 cc) was shaken in hydrogen at room temp and press. with pre-reduced PtO_2 catalyst. Absorption of H_2 ceased when the uptake was 1·0 mole. The product, isolated by filtration and evaporation, distilled at 136°/17 mm (0·50 g) (Found: C, 87·6; H, 12·4. $C_{15}H_{26}$ requires: C, 87·4; H, 12·6%), and did not react with tetranitromethane, Br_2 or $KMnO_4$ aq. Gas chromatography of the product, under the same conditions as for the original material, showed two sharp peaks with retention times similar to those of the original components. A similar reduction in glacial acetic acid (uptake 1·0 mole H_2) gave a different product, with four peaks in its gas chromatogram.

Reaction with hydrogen chloride. The hydrocarbon fraction (1·0 g) in dry ether (5 cc) was saturated at 0° with dry HCl gas. After some days at 0° a crystalline separation was noted; it was collected and recrystallized from ethanol, yielding cadinene dihydrochloride (0·07 g), m.p. 116–117° (Found: C, 63·7; H, 9·5; Cl, 25·6. Calc. for $C_{15}H_{26}Cl_2$: C, 64·9; H, 9·4; Cl, 25·6%), alone or mixed with an authentic specimen (lit.[16] m.p. 118·5°).

Oxidation. A suspension of the hydrocarbon fraction (4·1 g) in ice-water (80 g), $KMnO_4$ (7·2 g) and $(NH_4)_2SO_4$ (3·1 g) were shaken together for 5 hr. After passage of excess SO_2 and acidification the solution was extracted several times with $CHCl_3$, and the combined extracts shaken with $NaHCO_3$

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[14] P. G. Gassman, *Chem. & Ind.* 740 (1962).

[15] *Inter al.*, C. P. Dutta, *J. Indian Chem. Soc.* **18**, 233 (1941).

[16] Cf. F. Vonášek, V. Herout and F. Šorm, *Coll. Czech. Chem. Comm.* **25**, 919 (1960).

aq. The aqueous layer was separated and acidified at 0°, the liberated oil being isolated with ether. Evaporation of the dried extract afforded a viscous liquid (1·0 g) which was dissolved in pyridine (10 cc) and treated with semicarbazide hydrochloride (0·6 g) in the minimum amount of water. After being kept 10 days at 0° the crystalline deposit was collected (0·3 g) and recrystallized twice from ethanol, m.p. 221–222° (Found: C, 62·1; H, 8·8; N, 13·65. Calc. for $C_{16}H_{27}N_3O_3$: C, 62·1; H, 8·8; N, 13·6%), alone or mixed with an authentic sample of copaene ketonic acid semicarbazone.[3,4] The *2,4-dinitrophenylhydrazone* crystallized from ethanol in yellow needles, m.p. 221° (Found: C, 57·6; H, 6·4; N, 12·8. $C_{21}H_{28}N_4O_6$ requires: C, 58·3; H, 6·5; N, 12·95%). The neutral oxidation product was a viscous liquid, b.p. 112–114°/0·15 mm (2·0 g) (Found: C, 76·1; H, 9·7%), which showed strong IR absorption at 3700 cm^{-1} (in CCl_4) (OH), and may have been identical with the glycol (Calc. for $C_{15}H_{26}O_2$: C, 75·6; H, 11·0%) obtained by Semmler and Stenzel[3] by permanganate hydroxylation of copaene.

Monoterpene carbonyl fraction

Rechromatography on alumina of the fraction in solution in light petroleum (b.p. 30–40°), with elution with light petroleum (b.p. 30–40°)-benzene (1:1), and repeated fractional distillation *in vacuo*, afforded a clear, colourless liquid, b.p. 86–88°/10 mm, $[\alpha]_D^{20}$ −14·5° (*c*, 2·10) (Found: C, 80·0; H, 9·4. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·3%). Gas chromatography of the product using a 20% PEGA on 100–120 mesh Celite column at 100°, with a carrier gas flow rate of 25 cc/min showed that the fraction was substantially a single species, there being one major peak with a retention time of about 65 min. The product reduced Tollens' reagent in the cold during several hr, and gave a weak magenta colour with Schiff's reagent. IR spectrum (liquid film): ν_{max} 2703 (CH=O), 1661 ($\alpha\beta$ CH=O), 1608 ($\alpha\beta$ C=C), 1370, 1355, 1174, 1163 (all CMe_2) and 797 cm^{-1} ($R^1R^2C{=}CHR^3$), also weak shoulder at 1689 cm^{-1} ($\alpha\beta$ ketone). UV spectrum: λ_{max}^{MeOH} 243 mμ (ϵ 8000). The product formed a crystalline bisulphite compound and a 2,4-dinitrophenylhydrazone, which after chromatography in light petroleum (b.p. 60–80°)-benzene (1:1) over alumina separated, from ethanol in red needles m.p. 221–222° (dec) (Found: C, 58·2; H, 5·9; N, 16·9. Calc. for $C_{16}H_{18}N_4O_4$: C, 58·2; H, 5·5; N, 17·0%). A specimen of (+)-myrtenal was prepared by oxidation of (+)-α-pinene with selenium dioxide;[17] its 2,4-dinitrophenylhydrazone had m.p. 222° (dec) [lit.[17] m.p. 222° (dec)]. The IR spectra of this derivative and that of the above 2,4-dinitrophenylhydrazone were compared and found to be identical. The semicarbazone separated from ethanol in prisms, m.p. 224–225° (dec) (lit.[18] m.p. 225°).

An attempt to identify the very small amount of $\alpha\beta$-unsaturated ketone present in this fraction by removal of the aldehyde as its bisulphite adduct was unsuccessful.

Monoterpene alcohol fraction

The alcohol fraction was repeatedly fractionated *in vacuo*, yielding a colourless syrup, b.p. 95–97°/11 mm, $[\alpha]_D^{20}$ −45·8° (*c*, 2·0) (Found: C, 79·0; H, 10·6. Calc. for $C_{10}H_{16}O$: C, 78·9; H, 10·5%). Gas chromatography using a 20% Apiezon L on 100–120 mesh Celite column at 150°, with a carrier gas flow of 30 cc/min, showed that the fraction was mainly a single product, with a retention time of about 14 min. The product was unsaturated towards dil. $KMnO_4$ aq. IR spectrum (liquid film): ν_{max} 3472 (OH), 1647 (C=C), 1377, 1361, 1142, 1136 (all CMe_2) and 893 cm^{-1} ($R^1R^2C{=}CHR^3$). UV spectrum: λ_{max}^{MeOH} 209 mμ (ϵ 8800), λ_{max}^{hexane} 205 mμ (ϵ 8500). The IR spectrum was virtually identical with that of an authentic sample of (+)-myrtenol prepared by the oxidation of (+)-α-pinene with selenium dioxide.[18] The *p*-nitrobenzoate separated from light petroleum (b.p. 30–40°) in needles, m.p. 83–84°; the IR spectrum of this derivative (in CCl_4) was identical with that of an authentic sample of (+)-myrtenyl *p*-nitrobenzoate, m.p. 84–85°.[19] The *3,5-dinitrobenzoate* crystallized from light petroleum (b.p. 40–60°) in white plates, m.p. 121–122° (Found: C, 58·9; H, 5·6; N, 7·8. $C_{17}H_{20}N_2O_6$ requires: C, 58·6; H, 5·8; N, 8·0%). Oxidation of the fraction by shaking with activated MnO_2 in $CHCl_3$[9] afforded (−)-myrtenal, with virtually no unoxidized material.

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[17] H. E. Eschinazi and H. Pines, *J. Org. Chem.* **24**, 1369 (1959).

[18] G. Dupont, W. Zacharewicz and R. Dulon, *C.R. Acad. Sci. Paris* **198**, 1699 (1934); G. Dupont and W. Zacharewicz, *Bull. Soc. Chim. Fr.* 533 (1935).

[19] A. Stoll, E. Seebeck and D. Stauffacher, *Helv. Chim. Acta* **40**, 1205 (1957); W. Treibs, M. Mühlstädt, R. Megges and I. Klotz-Herdmann, *Liebigs Ann.* **634**, 118 (1959).

Middle boiling fraction of the oil

The residue remaining after distillation of the foregoing fractions was distilled, b.p. 122–176°/5 mm, and then redistilled through a 36 cm Vigreux column. From 463 g of the oil nine separate fractions were taken:

Fraction no.	b.p. (°/mm)	wt (g)	$[\alpha]_D^{20}$ in $CHCl_3$ (c, 2·10)	n_D^{20}
1	108–113/2	28	−10·8°	1·5028
2	113–115/2	34	−11·0°	1·5041
3	115–117/2	26	−10·9°	1·5052
4	117–120/2	26	−11·2°	1·5080
5	120–126/2	86	−15·1°	1·5103
6	114–117/0·4	30	−15·8°	1·5126
7	117–119/0·4	48	−17·3°	1·5134
8	119–122/0·4	32	−16·0°	1·5134
9	122–124/0·4	31	−15·3°	1·5147

Because of their similar optical rotations, refractive indices and IR spectra, fractions 1 to 4 inclusive, and 5 to 9 inclusive, were combined separately.

Fractions 1–4

The combined fractions 1–4 (21 g) in light petroleum (b.p. 40–60°) (500 cc) were chromatographed on alumina (300 g) and eluted with the same solvent (1200 cc). Evaporation yielded a residue (14·7 g) which was identical with the sesquiterpene hydrocarbon fraction described above. Further elution with light petroleum (b.p. 40–60°)–benzene (1:1) (1600 cc) gave a *sesquiterpene carbonyl fraction* (2·5 g). Final elution with benzene–ethanol (1:1) afforded a *sesquiterpene alcohol fraction* (2·5 g).

Sesquiterpene carbonyl fraction

Repeated distillation of the fraction afforded a colourless liquid, b.p. 136–138°/16 mm, which showed no reducing properties. Gas chromatography over 20% Apiezon L on Celite at 130° and IR measurements showed that it consisted of mainly one species, with two minor impurities. The 2,4-dinitrophenylhydrazone crystallized from ethanol in red needles, m.p. 231–232° (Found: C, 63·0; H, 6·6; N, 14·3. Calc. for $C_{21}H_{26}N_4O_4$: C, 63·3; H, 6·6; N, 14·1%). The m.p. was undepressed by admixture with the 2,4-dinitrophenylhydrazone, m.p. 228–229°, described by Naves and Ardizio[10] as a derivative of a ketonic component of *Cyperus scarosius*. UV spectrum: $\lambda_{max}^{CHCl_3}$ 397 mμ (ε 27,000) [lit.[10] $\lambda_{max}^{CHCl_3}$ 395 mμ (ε 28,200)]. Hydrolytic cleavage of the derivative (1·04 g) was effected by heating under reflux with acetone (180 cc) and conc. HCl aq (4·5 cc) for 45 min.[11] Stannous chloride dihydrate (4·5 g), conc. HCl aq (18 cc) and water (30 cc) were added and refluxing continued for 45 min under N_2. Removal of the acetone and isolation of the product with ether gave a pale yellow liquid, b.p. 104–106°/0·1 mm (0·4 g) (Found: C, 82·1; H, 9·8. $C_{15}H_{22}O$ requires: C, 82·5; H, 9·8%), $[\alpha]_D^{20}$ −26·6° (c, 3·50). A Kuhn-Roth estimation gave a value of 2·5 *C*-methyl groups. IR spectrum (liquid film): ν_{max} 1678 ($\alpha\beta$-unsaturated ketone C=O), 1634 (C=C, conjugated), 1387, 1376, 1181, 1166 (all CMe_2) and 890 cm^{-1} $R^1R^2C{=}CHR^3$, conjugated); $\varepsilon_{C=O}/\varepsilon_{C=C}$ = 6·5 (*transoid* C=C—C=O).[12] UV spectrum: λ_{max}^{MeOH} 206 (ε 5350) (C=C, heavily substituted) and 250 mμ (ε 10,500) ($\alpha\beta$-unsaturated ketone). Gas chromatography of the fraction at 150° on a column of PEGA (20%) on 100–120 Celite, and thin layer chromatography on silica gel, with development with $CHCl_3$ and location with I_2 vapour, showed the product to be substantially a single species, the $\alpha\beta$-unsaturated ketone *articulone*.

Catalytic hydrogenation. The ketone (0·55 g) in ethanol (10 cc) was shaken with pre-reduced Adams catalyst in H_2 at room temp. After 20 min absorption of H_2 (0·95 mole) ceased. Removal of the catalyst and evaporation gave *dihydroarticulone*, b.p. 150–151°/13 mm (0·49 g) (Found: C, 81·2; H, 10·9. $C_{15}H_{24}O$ requires: C, 81·1; H, 11·0%), $[\alpha]_D^{20}$ −14·8° (c, 2·30). IR spectrum (liquid film): ν_{max} 1715 cm^{-1} (saturated ketone C=O). UV spectrum: λ_{max}^{MeOH} 206 mμ (ε 5950) (C=C). The 2,4-*dinitrophenylhydrazone* separated from ethanol in yellow needles, m.p. 159–160° (Found: C, 63·3; H, 7·1; N, 13·6. $C_{21}H_{28}N_4O_4$ requires: C, 63·0; H, 7·05; N, 14·0%), $\lambda_{max}^{CHCl_3}$ 373 mμ

(ε 20,000). Shaking dihydroarticulone (1·43 g) in ethanol with 10% rhodium-on-carbon (1·4 g) in H_2 at room temp caused the uptake during 6 hr of a further mole of H_2. Working up in the usual way gave *tetrahydroarticulone*, b.p. 145°/9 mm (Found: C, 80·9; H, 11·7. $C_{15}H_{26}O$ requires: C, 81·0; H, 11·8%). IR spectrum (liquid film): ν_{max} 1715 cm^{-1} (saturated ketone C=O); no UV absorption above 200 mμ. The 2,4-dinitrophenylhydrazone crystallized from ethanol in orange-yellow needles, m.p. 195–196° (Found: C, 62·85; H, 7·0; N, 14·0. Calc. for $C_{21}H_{30}N_4O_4$: C, 62·7; H, 7·5; N, 13·9%), alone or mixed with a specimen described by Naves and Ardizio;[10] $\lambda_{max}^{CHCl_3}$ 370 mμ (ε 24,500) [lit.[10] $\lambda_{max}^{CHCl_3}$ 365–370 mμ (ε 24,700)].

Lithium aluminium hydride reduction. The ketone (2·05 g) in dry ether (30 cc) was added, with swirling, to an ice-cooled solution of $LiAlH_4$ (0·2 g) in dry ether (30 cc) during 15 min. After 16 hr at room temp the mixture was decomposed with ice-water in the presence of Celite. Evaporation of the dried ethereal decantate gave a viscous liquid (1·75 g), which was purified by chromatography on alumina, to give *articulol*, b.p. 124–125°/0·5 mm (1·60 g) (Found: C, 81·7; H, 11·2. $C_{15}H_{24}O$ requires: C, 81·8; H, 11·0%), $[\alpha]_D^{22.5}$ −13·7° (*c*, 5·9). IR spectrum (liquid film): ν_{max} 3600 (OH) and 1629 cm^{-1} (C=C). A crystalline 3,5-dinitrobenzoate could not be prepared, presumably because the product is a mixture of two epimerides.

Dehydrogenation of articulol. Articulol (0·55 g) and 30% Pd–C (0·55 g) were heated for 2 hr at 290–310°. Elimination of water occurred at ca. 240°. The product was isolated with ether, distilled, b.p. 130–140°/10 mm (0·38 g), and mixed with methanolic picric acid. The picrate which separated was recrystallized from ethanol, m.p. 114–115°, undepressed by admixture with an authentic specimen[15] of cadalene picrate, m.p. 114–115°. The X-ray powder photographs of the picrates were identical.

Reaction of articulone with magnesium methyl iodide, with dehydrogenation of the product. A Grignard reagent was prepared from Mg (0·5 g), methyl iodide (1·5 cc) and ether (10 cc), and cooled to 0° during the dropwise addition, during 5 min, of articulone (1·89 g; 1 mole) in dry ether (10 cc), with swirling. The mixture was refluxed for 1 hr, kept overnight, and decomposed by addition of NH_4Cl aq. The ether layer was separated, dried and evaporated, and the residual carbinol distilled, b.p. 114–124°/10 mm. IR spectrum (liquid film): ν_{max} 3650 cm^{-1} (OH), no carbonyl band. The carbinol (0·54 g) was heated with 30% Pd–C (0·25 g) at 260–280° for 6 hr, under N_2. The product, isolated with ether, distilled at 128–138°/9 mm (0·33 g). A portion of it was mixed with ethanolic picric acid, and the picrate collected and crystallized from ethanol, m.p. 107–108°, alone or mixed with an authentic sample of 8-methylcadalene picrate, m.p. 108°.[20] Another portion was converted into its 1,3,5-trinitrobenzene complex by a similar procedure. The derivative crystallized from ethanol in yellow needles, m.p. 117·5–118° (Found: C, 61·8; H, 5·5; N, 10·05. Calc. for $C_{22}H_{23}N_3O_6$: C, 62·2; H, 5·45; N, 9·9%), undepressed by admixture with authentic 8-methylcadalene 1,3,5-trinitrobenzene complex, m.p. 118–118·5°.[20] In both cases the identity was confirmed by X-ray powder photograph comparisons.

Ozonolysis of dihydroarticulone. Dihydroarticulone (1·02 g) in glacial acetic acid (40 cc) was ozonized at room temp for 1 hr, and the mixture then steam distilled. The aqueous distillate (ca. 500 cc) was mixed with ethanolic 2,4-dinitrophenylhydrazine sulphate, and kept for 12 hr. The derivative which separated was collected, dried, dissolved in light petroleum (b.p. 60–80°)–benzene (1:1), and chromatographed on alumina, with elution with the same solvent combination. Evaporation of the eluate yielded acetone 2,4-dinitrophenylhydrazone, yellow leaflets from ethanol, m.p. 125–126°, alone or mixed with an authentic specimen.

Sesquiterpene alcohol fraction

The fraction was re-chromatographed, and distilled three times, b.p. 120–122°/1 mm, $[\alpha]_D^{20}$ −22·0° (*c*, 5·04) (Found: C, 81·4; H, 10·7. $C_{15}H_{24}O$ requires: C, 81·8; H, 11·0%). IR spectrum (liquid film): ν_{max} 3550 (OH), 1645 (C=C), 1385, 1374, 1170, 1158 (all CMe_2) and 890 cm^{-1} ($R^1R^2C{=}CHR^3$). Gas chromatography on 20% Apiezon L on 100–120 mesh Celite at 150° showed that the fraction contained two major sesquiterpene alcohol components, with retention times, at a carrier gas flow rate of 30 cc/min, of 41 and 43·5 min. At least three minor components were present.

Manganese dioxide oxidation. The alcohol fraction (1·08 g) in $CHCl_3$ (100 cc) was shaken with activated MnO_2[9] (10 g) for 2 days. The system was filtered and the solvent removed. The residue (0·8 g) was dissolved in light petroleum (b.p. 40–60°) and chromatographed on alumina. Elution with

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[20] S. Dev, *Curr. Sci.* **16**, 377 (1947).

light petroleum (b.p. 40–60°)–benzene (1:1) gave, after evaporation, a liquid b.p. 100–104°/0·09 mm (0·55 g), the IR spectrum of which was virtually identical with that of articulone. The product was converted into its 2,4-dinitrophenylhydrazone in the usual manner. Chromatography of the crude product on alumina from light petroleum (b.p. 60–80°)–benzene (1:1), with elution with the same solvent mixture afforded, after evaporation and crystallization, articulone 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 231–232°.

Further elution of the chromatogram of the oxidation product with benzene–ethanol (5:1) yielded an alcoholic fraction b.p. 109–110°/0·1 mm (0·20 g), $[\alpha]_D^{20}$ −23·1° (*c*, 2·9) (Found: C, 81·1; H, 10·6. $C_{15}H_{24}O$ requires: C, 81·8; H, 11·0%). Thin layer chromatography on silica gel, with development with $CHCl_3$ and location with I_2, showed the presence of 4 components in the fraction, which was not further examined at this stage.

Fractions 5–9

Combined fractions 5 to 9 were chromatographed on alumina from light petroleum (b.p. 40–60°) solution. Careful elution as outlined in the previous section showed that these fractions were very similar in composition to the previous four fractions, being split up into hydrocarbon, ketone and alcohol fractions.

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