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CUPARENE AND CUPRENENE

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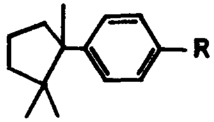
IN 1958, Erdtman et al.[1] isolated two sesquiterpenic hydrocarbons, widdrene and widdrene II, from heartwood of *Chamaecyparis thujoides*, *Biota orientalis* and various *Widdringtonia*, the former being identical with Thujopsene.[2] Widdrene II contains about 60% of an aromatic hydrocarbon named cuparene, whose structure was elucidated by Enzell and Erdtman[3] to be new ring system of sesquiterpene (A:R=Me). The present investigation concerned with the isolation of its biogenetic precursor, dihydrocuparene, to which we name cuprenene, and with the synthesis of *dl*-cuparene.



$R = CH_3$

A $R = COOH$

Neutral part of the essential oil from *Thujopsis dolabrata* Sieb. et Zucc. contains thujopsene, b.p. 123°/12 mm, $[\alpha]_D^{26}$ -106.4°, as a major component but,

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[1] H. Erdtman and B. R. Thomas, *Acta Chem. Scand.*, **12**, 267 (1958).

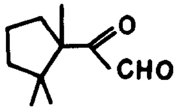
[2] H. Erdtman and T. Norin, *ibid.*, **13**, 1124 (1959).

[3] C. Enzell and H. Erdtman, *Tetrahedron*, **4**, 361 (1958).

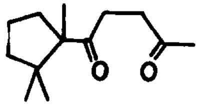
in fractional distillation, decrease of the absolute value of $[\alpha]_D$ was observed to reach a fraction (I) of b.p. 132/12 mm, $[\alpha]_D^{26}$ +63.8°, n_D^{26} 1.5112 d_4^{25} 0.9283, toward the end of thujopsene fraction. The fraction (I),[4] λ_{max}^{MeOH} 265 mμ (logε 3.41), absorbs 2 molar equivalents of hydrogen (Pd in Ethanol) and 1.2 mole of bromine (vigorous evolution of hydrogen bromide was observed).

Heating of (I) with chloranil or selenium dioxide gave colorless oil (II), b.p. 131/12 mm, n_D^{26} 1.5195, $[\alpha]_D^{26}$ +64.0°, d_4^{25} 0.9350, IR spectrum of which is completely identical with that of cuparene reported by Erdtman.[3] That the fraction (I) is closely related with cuparene is confirmed by oxidation studies. Nitric acid oxidation of (I) gave terephthalic acid and cuparenic acid (III) (A:R=COOH)[3], m.p. 163°(S-p-Bromobenzylthiouronium salt, $C_{23}H_{29}O_2N_2SBr$, m.p. 187°. p-Bromophenacyl ester, $C_{23}H_{25}O_3Br$, m.p. 125°), whereas ozonolysis (175°) afforded, besides oxalic acid and formaldehyde, d-camphonanic acid (IV), m.p. 191°. IR spectra of (III) and (IV) are identical with those reported.[3]

The neutral product of ozonolysis was consisted of two components: 1) Oil (V), $C_{10}H_{26}O_2$ (2,4-dinitrophenylhydrazone, m.p. 186°) volatile with steam. 2) Oil (VI) $C_{13}H_{22}O_2$ (monosemicarbazone, m.p. 248°) nonvolatile with steam.



V



VI

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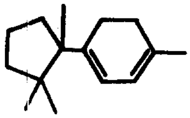
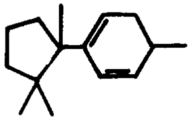
[4] Molecular formula was assumed to be $C_{15}H_{24}$.

Whilst the structure of (V) was assumed to be 1,2,2-trimethylcyclopentylglyoxal from positive silver mirror test, positive Fehling test and formation of d-camphonanic acid by nitric acid oxidation, the structure of (VI) was proposed to be 1-(1',2',2'-trimethylcyclopentyl)-pentan-1,4-dione from analysis of semicarbazone, positive iodoform test and formation of d-camphonanic acid upon nitric acid oxidation. (V) and (VI) gives only monocarbonyl derivatives showing large steric hindrance on the second carbonyl group.

Since it is known that cuparene is stable[3] under ozonization condition used, one could draw a conclusion that the fraction (I) contains dihydrocuparenes, to which the authors wish to attribute the name cuprenene. There might be two cuprenenes in the fraction (I), one of which, α-cuprenene (B), afforded (VI), the other, β-cuprenene (C), giving compound (V). However, methylsuccinic acid, which should be resulted from β-cuprenene, was failed to be detected.



B



C

The fraction (I) also contains some cuparene, presence of which could be revealed from absorption bands at 1520, 810 cm^{-1} in its IR spectrum. Cuprenenes easily undergo dehydrogenation on mild oxidation with permanganate, chromic acid or ozone or even on standing in air. The fact is shown from the disapearance of bands at 1640, 886 cm^{-1} in its IR spectrum and change in UV spectrum (from λ_{max}^{MeOH} 265 mμ (log ε 3.41) to λ_{max}^{MeOH} 218, 265 mμ (log ε 3.88, 2.53)) and separation of some water on every distillation of the fraction.

It might be appropriate to suppose that cuparene is a secondary product and cuprenene is the real constituent of Thujopsis dolabrata.

1,2,2-trimethyl cyclopentylbromide, m.p. 43°, obtained from d-camphonanic acid by Hansdiecker reaction, was converted to lithio-compound and condensed with p-bromotoluene to give dl-cuparene. The identity was established by the comparison of IR spectra, N.M.R spectra (in $CHCl_3/CCl_4$), gas chromatography (with Reoplex 400- Celite 545, 190°C, He 50 ml/min retention time 204 sec) and by the formation of dl-cuparenic acid (S-p-Bromobenzylthiouronium salt, m.p. 182°).

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