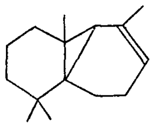
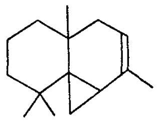
UDC 547.913.02 : 582.475

Structure of Thujopsene

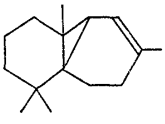
Thujopsene,[1] the principal constituent of the essential oil of *Thujopsis dolabrata* SIEB. ET ZUCC., is a liquid hydrocarbon, $C_{15}H_{24}$, with an ethylenic double bond. Investigation on this hydrocarbon was initiated by its ozonolysis and permanganate oxidation[2] which suggested the presence of a new tricyclic ring system.[3] In 1958, Kobayashi, *et al.*[4] suggested the structure (A) for this oil from their results of dehydrogenation. Erdtman, *et al.*, after proposing the same structure (A) for their widdrene,[5] which turned out to be identical with thujopsene,[6] recently suggested the modified structure (B) mainly on the basis of their hydrogenation experiments.[7]



(A)



(B)



(C)

An alternative structure (C) was, however, proposed by Shishido, *et al.* from the consideration of biogenesis and was said to be supported by almost all of the known reactions of the hydrocarbon.[8] Such a publication made it desirable to record some of the observations gained in this laboratory in favor of the structure (B) to (A) and (C), although the evidences provided by Erdtman, *et al.* seemed to be quite convincing and the present writers' results coincided with the earlier reports in many respects.

First of all, the structure (C) could be eliminated from the following evidences : (i) The keto acid[2,6,9] (II), m.p. 164°; UV[*1] λ 282 mμ; IR ν 1691∼1700 cm^{-1} (2,4-dinitrophenylhydrazone, m.p. 197°; UV λ 234, 370 mμ), obtained by ozonolysis or permanganate oxidation of thujopsene (I), gives, on treatment with mineral acid at 0°, a keto-γ-lactone[3,9] (III), m.p. 56°; UV λ 270 mμ; IR ν 1776, 1720 cm^{-1} (2,4-dinitrophenylhydrazone, m.p. 164°; UV λ 228, 363 mμ). While (II) exhibits no band around 1420 cm^{-1} in its IR spectrum, (III) has a sharp medium band at 1419 cm^{-1} due to $-CH_2CO-$.[10] (ii) There are two isomeric monomethyl esters of the dicarboxylic acid[3,6,9] (IV), m.p. 212°, obtained by hypobromite oxidation of (II). One is the methyl ester (V), m.p. 59∼60°, formed by either mild esterification[9] of (IV) or hypobromite oxidation[11] of methyl ketocarboxylate. The other methyl ester (VI),[3] $C_{15}H_{24}O_4$,[*2] m.p. 114∼115°, is obtained by partial hydrolysis of dimethyl dicarboxylate,[2,6] m.p. 73°.

[*1] UV spectra were measured in methanol and IR spectra were taken in the form of KBr disks.

[*2] All analytical values are in good agreement with the molecular formulae.

1) J. Kawamura : Bull. Govt. Experiment. Station, **30**, 69(1930).

2) T. Ozeki, S. Seto, T. Nozoe : Paper presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957.

3) T. Nozoe, T. Ozeki, S. Seto : Paper presented at the 1st Symposium on Terpene, Perfumery and Essential Oil Chemistry, Osaka, October, 1957.

4) H. Kobayashi, S. Nagahama, S. Akiyoshi : Bull. Chem. Soc. Japan, **32**, 203(1959).

5) H. Erdtman, R. B. Thomas : Acta Chem. Scand., **12**, 267(1958).

6) H. Erdtman, T. Norin : *Ibid.*, **13**, 1124(1959).

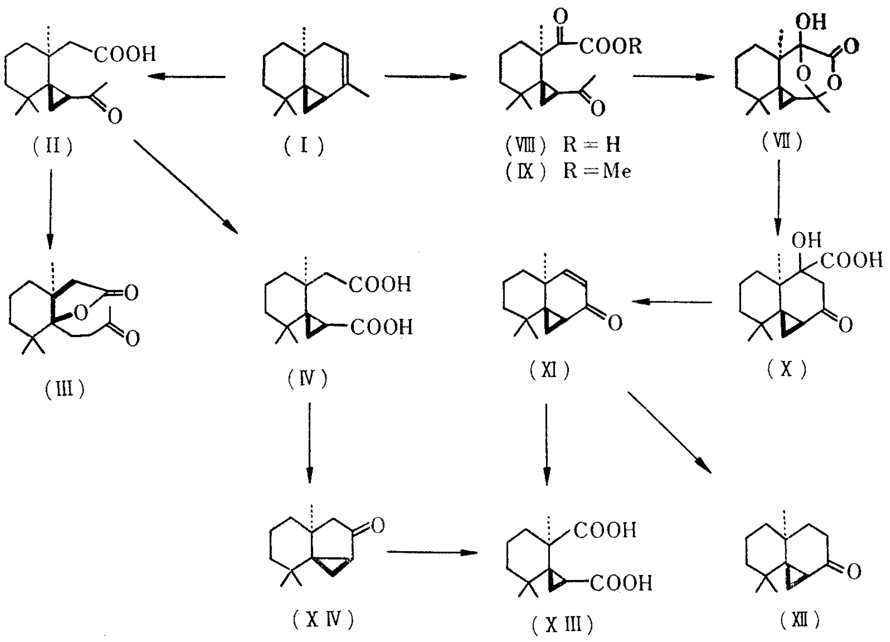
7) *Idem* : Chem. & Ind. (London), **1960**, 622.

8) K. Shishido, H. Nozaki : J. Org. Chem., **25**, 875(1960).

9) S. Akiyoshi, S. Nagahama : Bull. Chem. Soc. Japan, **30**, 886(1957).

10) R. N. Jones, A. R. Cole, B. Nolin : J. Am. Chem. Soc., **74**, 5662(1952); B. Nolin, R. N. Jones : *Ibid.*, **75**, 5626(1953).

11) T. Nozoe, H. Takeshita, H. Akiyama : Paper read at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.



This is an indication of considerable steric hindrance in one of the hydroxyl groups in (IV). (ii) Permanganate oxidation of (I) affords, besides (II), a lactol-ketal[11),*3] (VII), m.p. 123°; IR ν 3370, 3050, 1758 cm^{-1}, presumably formed via diketocarboxylic acid (VIII), methylation with diazomethane providing a methyl diketocarboxylate (IX), $C_{16}H_{24}O_4$, m.p. 89°; IR ν 3020, 1720, 1710, 1690 cm^{-1}. Alkaline treatment of (VII) yields a hydroxyketocarboxylic acid[3,9)] (X), m.p. 212°, which, after thermal dehydration followed by decarboxylation with copper and quinoline, gives an unsaturated ketone (XI), $C_{14}H_{20}O$, m.p. 75°; UV λ 222, 313 mμ; IR ν 1672, 1625 cm^{-1} (2,4-dinitrophenylhydrazone; two forms, m.p. 173~174° and m.p. 177~178°, UV λ (both forms) 256, 387 mμ). Catalytic hydrogenation of (XI) gives a saturated ketone (XII), $C_{14}H_{22}O$, m.p. 105°; UV λ 280 mμ; IR ν 3060, 1691 cm^{-1}; $[\alpha]_{306}$ +4890° (2,4-dinitrophenylhydrazone, m.p. 187°; UV λ 235, 369 mμ), while ozonolysis of (XI) yielded nordicarboxylic acid (XIII), $C_{13}H_{20}O_4$, m.p. 212°, also obtained from (III) through pyroketone[3,12)] (XIV), m.p. 120°; UV λ 279 mμ; IR ν 3070, 1724 cm^{-1}; $[\alpha]_{302}$ +7030°.

These experimental results and observations clearly indicate the conjugation of a cyclopropane ring with carbonyl group[13)] and not with carboxyl group in (II), excluding the structure (C). Furthermore, (II) exhibits a large Cotton effect ($[\alpha]_{308}$ −2707°) whereas (III) has a small one ($[\alpha]_{280}$ −630°), giving an additional evidence that the asymmetric center is located close to the keto group in (II).[14)]

Choice between the structures (A) and (B) was ingeneously demonstrated by Erdtman and Norin,[7)] and it is simply pointed out that the weak band around 3050 cm^{-1}, due to $-CH_2-$ in cyclopropane,[15)] is clearly observed in the infrared spectra of (VII), (IX), (XIII), and (XIV), whereas that of (III) completely lacks this band.

All of these evidences ultimately lead to the structure (B), including the configuration of cyclopropane ring originally suggested by Erdtman and Norin.[7)]

[*3] Referred to the hydroxylactone in reference (9).

12) S. Nagahama, H. Kobayashi, S. Akiyoshi : Bull. Chem. Soc. Japan, **32**, 365(1959).

13) J. M. Kolz : J. Am. Chem. Soc., **66**, 88(1944); J. D. Roberts, C. Green : *Ibid.*, **68**, 214(1946)

14) C. Djerassi, L. E. Geller : *Ibid.*, **81**, 2789(1959).

15) A. R. H. Cole : J. Chem. Soc., **1954**, 3807, 3810.