Tetrahedron Letters No. 42, pp 3681 - 3684, 1974. Pergamon Press. Printed in Great Britain.

TAYLORIONE, A NOVEL CARBON SKELETAL SESQUITERPENE KETONE FROM THE LIVERWORT, *MYLIA TAYLORII* (HOCK.) GRAY1)

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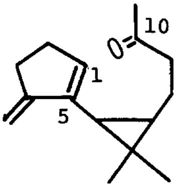
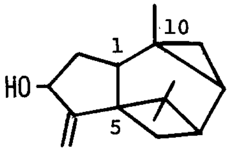
(Received in Japan 29 June 1974; received in UK for publication 12 September 1974)

From *Mylia taylorii* (Hock.) Gray (Japanese name Katauroko-goke), which is a leafy liverwort belonging to the *Jungermanniaceae*, a sesquiterpene ketone with a novel carbon skeleton have been isolated. We propose the name taylorione for this ketone and describe herewith the evidences for the proposed structure (I).

Taylorione(I), 2,4-DNP, mp 131-132°; $[\alpha]_D$ -28.1°(c 1.52),2) was isolated as a colorless oily substance by eluting the hexane extract of the plant over silica gel with a mixed solvent of hexane and ethyl acetate(4 : 1) together with myliol(II) which had been obtained from the same liverwort by Benešová et al.3)



(I)

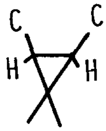


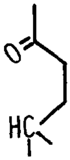
(II)

The compound(I) was analyzed for $C_{15}H_{22}O$(M^+ 218), and UV, IR and NMR spectral data indicated that it contained a gem-dimethyl($\nu_{max}^{CCl_4}$ 1379, 1363 cm^{-1}; $\delta_{ppm}^{CCl_4}$ 0.90, 1.15, each 3H, s), an acetyl(ν 1726, δ 2.06, 3H, s), three active methylenes(ν 1430, 1414; δ 2.2-2.6, 6H) connected to C-O and/or C-C double bonds and an exo double bond conjugated with a tri-substituted double bond(λ_{max}^{EtOH} 243 nm, ε 14900; ν 3085, 1635, 868, 854; δ 4.66, 4.75, 5.85, each 1H, br.s). When the ketone(I) was hydrogenated over PtO_2 in AcOH, it furnished a saturated tetrahydro ketone(III), $C_{15}H_{26}O(M^+ 222)$; $[\alpha]_D$ -22.3°(c 2.88), which contained a newly formed secondary methyl($\delta_{ppm}^{CCl_4}$ 0.90, 3H, d, J=8.0) and an active methylene ($\nu_{max}^{CCl_4}$ 1420 cm^{-1}; δ 2.40, 2H, t, J=8.0) together with two originally present groups of gem-dimethyl(ν 1385, 1368; δ 0.94, 1.02, each 3H, s) and acetyl(ν 1730, 1168; δ 2.03, 3H, s). Thus, it is certain that the compound(I) is a bicyclic sesquiterpene ketone containing a conjugated diene system.

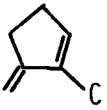
Although the NMR spectrum of tetrahydro taylorione(III) showed clearly the presence of two cyclopropane protons(δ 0.2-0.5, 2H), an absorption band attributable to cyclopropane methylene was not observed in the IR spectrum. This fact indicates taylorione(I) and tetrahydro taylorione(III) to have such a tetra-substituted cyclopropane system, partial structure A, as it consists of two methines and a quarternary carbon atom bearing the gem-dimethyl group. In tetrahydro taylorione(III), also, it was certain that the acetyl group connected to a saturated carbon chain, because the active methylene(ν 1420) adjacent to the carbonyl group appeared as triplet(J=8.0) centerring at δ 2.40. The length of this connecting carbon chain was determined as a series of degradation reaction: tetrahydro taylorione(III) was submitted to Baeyer-Villiger reaction with CF_3CO_3H and the ester thus obtained was then hydrolyzed with KOH to give a bis-nor primary alcohol(IV), $C_{13}H_{24}O(M^+ 196)$; $[\alpha]_D$ -23.6°(c 0.79); $\nu_{max}^{CCl_4}$ 3630, 3330, 1050 cm^{-1}, which was converted into an acid(V), $C_{13}H_{22}O_2(M^+ 210)$; $[\alpha]_D$ -40.6°(c 0.32); $\nu_{max}^{CCl_4}$ 3400-2500, 1710 cm^{-1}, by Jones oxidation. As to the degradation products, the carbinol methylene($\delta_{ppm}^{CCl_4}$ 3.56, 2H) of the bis-nor alcohol(IV) showed a triplet(J=7.0) and the active methylene(ν 1410; $\delta_{ppm}^{CCl_4}$ 2.29, 2H) of the acid(V) a doublet(J=7.0). These evidences indicate that, in taylorione (I) and tetrahydro taylorione(III), the acetyl group connects with a methine group with a distance of two methylene units, partial structure B.

The residual portion of the taylorione molecule, on the basis of the molecular formula and the above-mentioned spectroscopic evidences, was deduced to contain the exo double bond conjugated with a tri-substituted double bond and two active methylenes adjacent to the double bonds. For such system, three

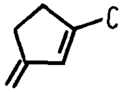




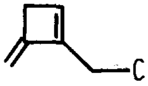
B



C-a

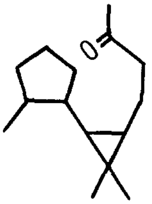


C-b

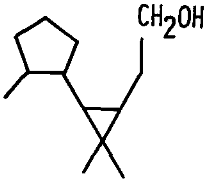


C-c

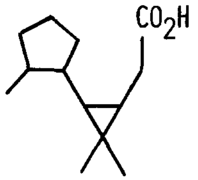
partial structures, C-a, C-b and C-c, were possible, but only C-a was picked up by a series of the following reaction: taylorione(I) was took up one molar equivalent of hydrogen in catalytic hydrogenation over Pd-C in EtOH to give a dihydro ketone(VI), $C_{15}H_{24}O$(M^+ 220), $[\alpha]_D$ -25.0°(c 0.88); $\nu_{max}^{CCl_4}$ 1725, 1415, 1380, 1363, 1165 cm^{-1}, which contained a tetra-substituted double bond bearing a methyl group($\delta_{ppm}^{CCl_4}$ 1.67, 3H, br.s). The formation of such a vinylic methyl is expected in the 1,4-addition of hydrogen to the conjugated diene system of the taylorione molecule, and the value of the UV absorption maximum(λ_{max}^{EtOH} 212 nm, ε 5900) suggests that the tetra-substituted double bond is in the conjugation with the cyclopropane ring. The dihydro ketone(VI) was then oxidized with osmic acid to give a glycol(VII), $C_{15}H_{26}O_3$($[M-H_2O]^+$ 236); $[\alpha]_D$ -28.4°; $\nu_{max}^{CCl_4}$ 3500, 1723, 1410, 1380, 1360, 1165 cm^{-1}; $\delta_{ppm}^{CCl_4}$ 0.1-0.5(2H, complex), 1.05, 1.17(each 3H, s), 1.23(3H, s), 2.13(3H, s), 2.47(2H, t, J=7.0), 2.90(2H, exchangeable



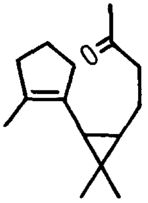
(III)



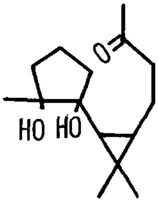
(IV)



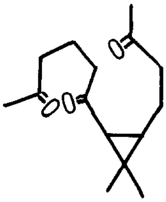
(V)



(VI)



(VII)



with D_2O), which, by means of glycol fission with periodic acid, was lastly converted into a tri-ketone(VIII), $C_{15}H_{24}O_3$(M^+ 252); $[\alpha]_D$ -50.2°. The tri-ketone(VIII) thus obtained possessed a ketone group conjugating a cyclopropane ring($\lambda_{max}^{isooct.}$ 203 nm, ε 3000; $\nu_{max}^{CCl_4}$ 1695 cm^{-1}; $\delta_{ppm}^{CCl_4}$ 0.9-1.4, 2H) and two acetyl groups(ν 1725; δ 2.08, 6H, s) together with a gem-dimethyl(ν 1385, 1380, 1370; δ 1.16, 6H, s), three active methylenes(ν 1420; δ 2.1-2.6, 6H) and two aliphatic methylenes(ν 1450; δ 1.5-2.0, 4H).

From the above evidences, the gross structure of taylorione isolated from the liverwort can be expressed by formula I. This novel carbon skeleton may be biosynthesized from an aromadendrene-type precursor which is common to co-occurring myliol(II) via the oxidative cleavage of the C_1-C_{10} bond. The investigation on absolute configuration and biogenesis of this ketone are under progress.

The authors wish to express their gratitude to Dr. Mikio Hara, Kôchi University, for collection and identification of the liverwort, and they are grateful to the Japanese Ministry of Education for financial support of this work.

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