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ISOLATION OF TWO NEW *ENT*-KAURANE CLASS DITERPENOIDS FROM *PORELLA DENSIFOLIA* (LIVERWORT)

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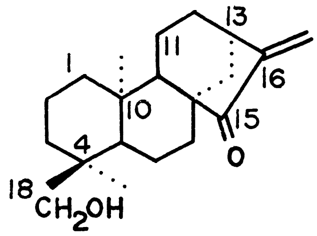
Two kinds of new diterpene keto-alcohols were isolated from *Porella densifolia*. The structures including absolute configurations were elucidated to be *ent*-18-hydroxykauren-15-one(I) and (16R)-*ent*-18-hydroxykauran-15-one(II) in combination of chemical reaction and spectroscopic analysis.

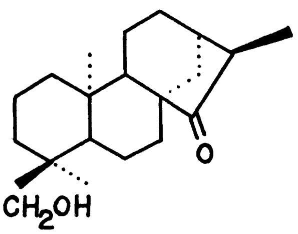
The liverworts(hepaticae) described as a unique group in the plant kingdom contain some oil bodies characteristic of the species in each cell of the plant bodies growing from the gametophytes(haploidal). From *Porella densifolia* (Steph.) Hatt., a liverwort distributed predominantly in a zone of lime stone, two new *ent*-kaurane class diterpenoids were now isolated together with three known diterpenoids of *ent*-11α-hydroxykauren-15-one(III), (16R)-*ent*-11α-hydroxykauran-15-one(IV)[1-3] and *ent*-kauren-18-oic acid(V),[4,5] and the structural determination was carried out. The present paper deals with the experimental results for the proposed structures.

Diterpenoid I, $C_{20}H_{30}O_2$(M^+ 302); mp 121-122 °C; $[\alpha]_D$ -147°,[6] and diterpenoid II, $C_{20}H_{32}O_2$(M^+ 304); mp 176.5-177.5 °C; $[\alpha]_D$ -82.5°,[7] were isolated from the methanol extract in combination of elution chromatography and preparative TLC.

The spectral data indicated diterpenoid I to be a tetracyclic one containing a cyclopentanone conjugated with an exomethylene, two tertiary methyls and a tertiary hydroxymethyl. The catalytic hydrogenation of I over Pd-C in EtOAc gave a dihydro-derivative, $C_{20}H_{32}O_2$; mp 176.5-177.5 °C; $[\alpha]_D$ -87.3°, whose physical



(I)



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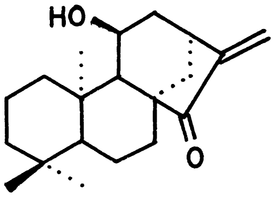
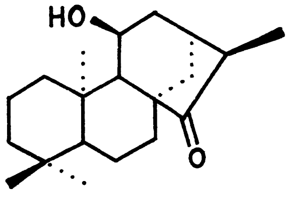
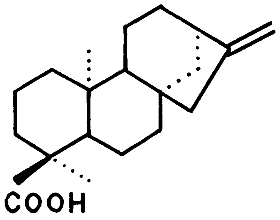


(III)



(IV)

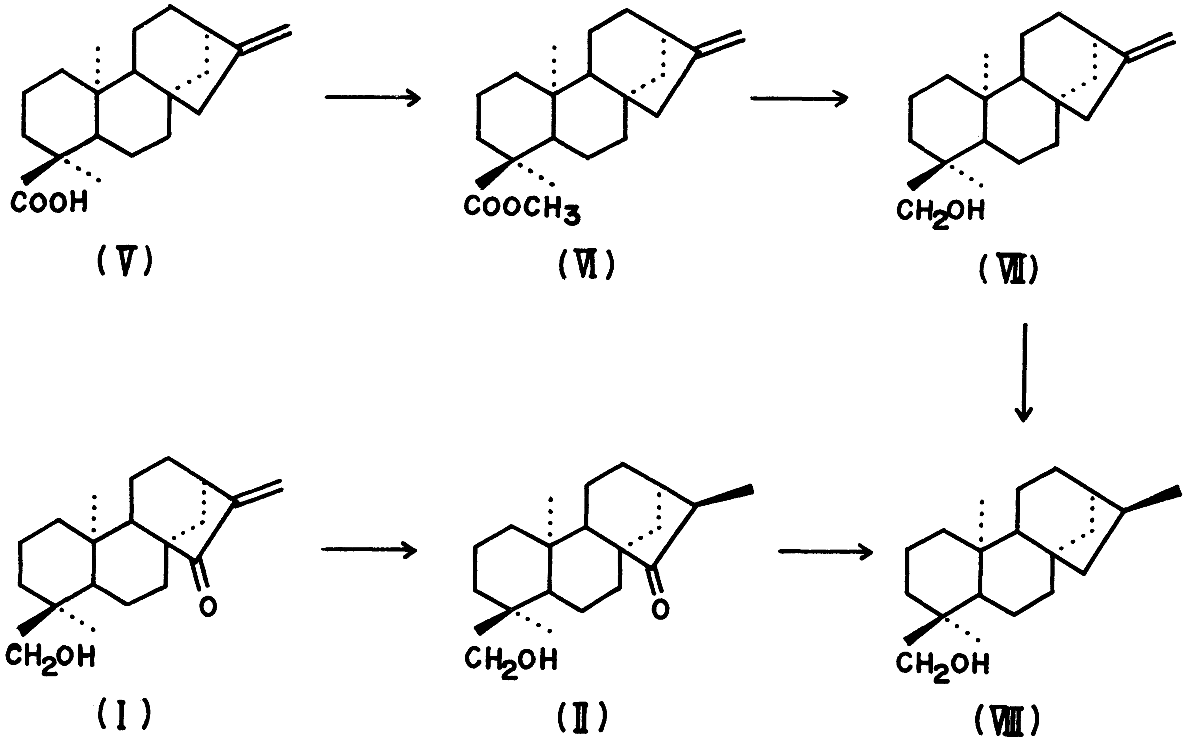


(V)

constants were coincident with those of diterpenoid II co-occurring in the same liverwort. Accordingly, both new diterpenoids are certain to have the same carbon skeleton, which, from the spectral information, may be characterized as kaurane or phyllocladane type bearing the carbonyl at C-15. Furthermore, the hydroxymethyls of I and II appeared respectively at δ_{CDCl_3} 3.09 and 3.43(each 1H, d, J=11) and at δ_{CDCl_3} 3.08 and 3.42(each 1H, d, J=11),8) and their tertiary methyls(I: δ_{CDCl_3} 0.79, 1.14; $\delta_{C_5H_5N}$ 0.83, 1.08; II: δ_{CDCl_3} 0.78, 1.12; $\delta_{C_5H_5N}$ 0.83, 1.06) did not show the pyridine-induced solvent shift.9) These facts suggested that the hydroxymethyls of these compounds are located on C-4 of the above-mentioned carbon skeleton with equatorial configuration.

For the final confirmation of the structures and absolute configurations of these new diterpenoids, diterpenoid II was connected with the co-occurring *ent*-kauren-18-oic acid. The acid, after being converted with diazomethane to a methyl ester(VI), was reduced by $LiAlH_4$ to afford *ent*-kaurenol(VII)10) which was catalytically hydrogenated over PtO_2 in AcOEt. (16R)-*ent*-Kauran-18-ol(VIII)11) thus obtained was identical with the deoxo-derivative, $C_{20}H_{34}O$; mp 125.5-126.5 °C; $[\alpha]_D$ -46.2°,12) which was prepared from naturally occurring diterpenoid II by a modified Wolff-Kishner reduction.13)

Thus, the structures including absolute configurations of the two diterpenoids were respectively determined to be *ent*-18-hydroxykauren-15-one and (16R)-*ent*-18-hydroxykauran-15-one and should be represented by formulae I and II. They contain the hydroxymethyl with equatorial configuration on C-4 of *ent*-kaurane skeleton, and such configurations are rare in kaurane and phyllocladane class diterpenoids.[14]



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5) The physical constants of III, IV and V were as follows; III: $C_{20}H_{30}O_2$; mp 140-141 °C; $[\alpha]_D$ -165°; IV: $C_{20}H_{32}O_2$; mp 185-186 °C; $[\alpha]_D$ -76.1°; V: $C_{20}H_{30}O_2$; mp 150-151 °C; $[\alpha]_D$ -63.2°.

6) The spectral data of I: ν_{CCl_4} 3625, 3420, 1725, 1644, 1050 cm^{-1}; δ_{CDCl_3} 0.79, 1.14(each 3H, s), 3.09, 3.43(each 1H, d, J=11), 5.23, 5.93(each 1H, br.s); λ_{EtOH} 232 nm(ε 5.08x10^3).

7) The spectral data of II: ν_{CCl_4} 3625, 3435, 1730, 1030 cm^{-1}; δ_{CDCl_3} 0.78, 1.12 (each 3H, s), 1.10(3H, d, J=6.5), 3.09, 3.43(each 1H, d, J=11).

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11) The data of VI, VII and VIII derived from V were as follows; VI: $C_{21}H_{32}O_2$; mp 118-119 °C; $[\alpha]_D$ -47.6°; ν_{CCl_4} 1730, 1655, 1240, 875 cm^{-1}; δ_{CDCl_3} 1.08, 1.18, 3.67(each 3H, s), 4.80(2H, br.s); VII: $C_{20}H_{32}O$; mp 105-106 °C; $[\alpha]_D$ -79.4°; ν_{CHCl_3} 3615, 3425, 1660, 1035, 875 cm^{-1}; δ_{CDCl_3} 0.78, 1.09(each 3H, s), 3.06, 3.42(each 1H, d, J=11), 4.78(2H, br.s); VIII: $C_{20}H_{34}O$; mp 126-127 °C; $[\alpha]_D$ -44.9°; ν_{CHCl_3} 3620, 3445, 1030 cm^{-1}; δ_{CCl_4} 0.73, 1.04(each 3H, s), 1.00(3H, d, J=6.5), 2.96, 3.43(each 1H, d, J=1o.5).

12) The spectra of the deoxo-derivative(VIII): ν_{CCl_4} 3630, 3400, 1030 cm^{-1}; δ_{CCl_4} 0.73, 1.05(each 3H, s), 1.02(3H, d, J=6.5), 2.96, 3.35(each 1H, d, J=10.5).

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