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(-)-ISOBICYCLOGERMACRENAL, A NOVEL SESQUITERPENOID OF *ENT*-
ISOBICYCLOGERMACRENE GROUP FROM THE LIVERWORT *LEPIDOZIA VITREA*

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(-)-ISOBICYCLOGERMACRENAL, A NOVEL SESQUITERPENOID OF *ENT*-ISOBICYCLOGERMACRENE GROUP FROM THE LIVERWORT *LEPIDOZIA VITREA*

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A novel sesquiterpene aldehyde, (-)-isobicyclogermacrenal, was isolated from *Lepidozia vitrea*, and its structure and absolute configuration were shown to be *ent*-isobicyclogermacren-14-al on the basis of the chemical and spectral evidence.

In the course of our investigation on terpenoids from the liverworts (Hepaticae),²⁾ a novel sesquiterpene aldehyde named (-)-isobicyclogermacrenal was isolated from a methanol extract of the leafy liverwort *Lepidozia vitrea* Steph. The structure and absolute configuration was determined as the formula(1), and we here describe the chemical and spectral evidence for the proposed structure.

(-)-Isobicyclogermacrenal(1), C₁₅H₂₂O(M⁺ 218); [α]_D -168°(c 1.0, CHCl₃), was characterized to be a bicyclic sesquiterpenoid containing an aldehyde conjugated with a trisubstituted double bond [λ (EtOH) 261 nm(ϵ 11600); ν (CCl₄) 2810, 2705, 1685, 1624 cm⁻¹; δ (CDCl₃) 6.28(1H, d, J=9.0 Hz), 9.25(1H, s)], a trisubstituted double bond [ν 860 cm⁻¹; δ 5.06(1H, m)] bearing a methyl group [δ 1.25(3H, d, J=1.5 Hz)], a cyclopropane ring [δ 0.5-0.9(2H, complex)] and a gem-dimethyl [ν 1387, 1380 cm⁻¹; δ 1.18, 1.21(each 3H, s)]. The spectra resembled those of bicyclogermacrene³⁾ and isobicyclogermacrene⁴⁾ prepared by isomerization of the former, apart from the presence of an aldehyde group.

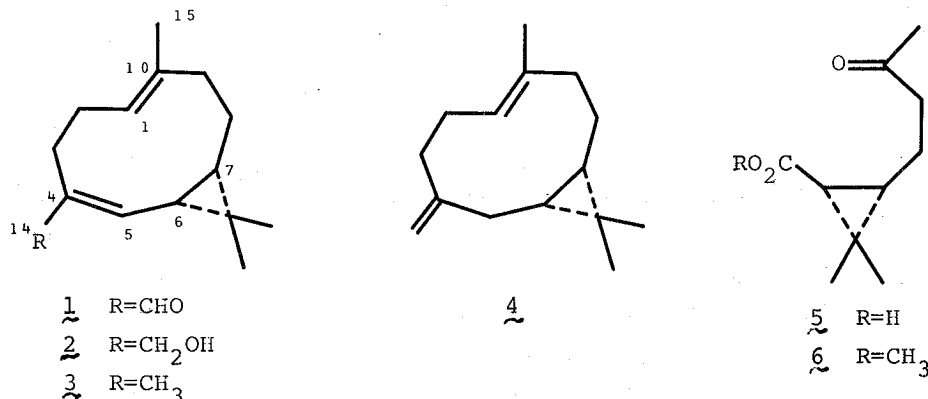
Now, 1 was reduced with LiAlH₄ in ether to give an alcohol(2), C₁₅H₂₄O(M⁺ 220); mp 86.5-88 °C; [α]_D +21°(c 1.1, CHCl₃), whose structure was supported by the off-resonance ¹³C-NMR spectrum(3 singlets, 4 doublets, 5 triplets and 3 quartets).⁵⁾ By treatment of 2 with C₅H₅N-SO₃ and followed by LiAlH₄ in ether it was then transformed into a polar hydrocarbon(3), C₁₅H₂₄(M⁺ 204); [α]_D +15°(c 1.0, CHCl₃), as well as a less polar hydrocarbon(4), C₁₅H₂₄(M⁺ 204); [α]_D +4.0°(c 1.0, CHCl₃), in a ratio of 2 : 1. The major sesquiterpene hydrocarbon was identified as isobicyclogermacrene, excluding the absolute configuration, by a comparison of the IR and ¹H-NMR spectra with those of the authentic specimen.⁴⁾ The geometries of two double bonds were also confirmed to be 4-*cis* and 1(10)-*trans* on the basis of NOE of the original aldehyde(1); when the signal of the aldehyde proton(δ 9.25) was saturated by double irradiation, the integrated intensity of the 5-H signal

(δ 6.28) increased and the value was measured as about 14 %. However, saturation of the 10-Me (δ 1.25) caused no increase in the intensity of the 1-H signal (δ 5.06).

In order to establish the absolute configuration, 2 was submitted to ozonolysis in EtOAc and the resulting ozonide was oxidatively decomposed with H_2O_2 to afford an acid (5), $C_{10}H_{16}O_3$ ($[M-58]^+$ 126); $[\alpha]_D -18^\circ$ (c 1.2, $CHCl_3$), which was then converted into a methyl ester (6), $C_{11}H_{18}O_3$ (M^+ 198); $[\alpha]_D -23^\circ$ (c 1.7, $CHCl_3$). The spectroscopic properties and signs of the optical rotations of both compounds (5 and 6) coincided with those of the corresponding acid and ester derived from (-)-taylorione, *ent*-1,10-seco-aromadendra-1(5),4(15)-dien-10-one, respectively.⁶⁾

Accordingly, the structure and absolute configuration of (-)-isobicyclogermacrenal should be represented by *ent*-isobicyclogermacren-14-al or (1*E*,4*E*)-*ent*-bicyclogermacra-1(10),4-dien-14-al (1). This is the first example of the naturally occurring isobicyclogermacrene sesquiterpenoid, and the compound inhibits the growth of rice at concentration of 50 ppm.

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References and Notes

- 1) The present address: Department of Chemistry, Faculty of Science, Okayama University of Science, Ridai-cho, Okayama 700.
- 2) The previous paper: A. Matsuo, H. Nozaki, K. Atsumi, H. Kataoka, M. Nakayama, Y. Kushi, and S. Hayashi, *J. Chem. Soc., Chem. Commun.*, 1979, in press.
- 3) K. Nishimura, N. Shinoda, and Y. Hirose, *Tetrahedron Lett.*, 1969, 3097.
- 4) K. Nishimura, I. Horibe, and K. Tori, *Tetrahedron*, 29, 271 (1973).
- 5) The spectral data of the new compounds (2 and 4) derived from 1 were as follows.
2: $\nu(CCl_4)$ 3620, 3400, 1670, 1390, 1380, 1218, 1080, 992, 860 cm^{-1} ; $\delta(CDCl_3)$ 1.03, 1.07 (each 3H, s), 1.36 (3H, d, $J=1.5$ Hz), 3.99 (2H, br.s), 5.12 (1H, m), 5.22 (1H, d, $J=8.0$ Hz); $\delta_C(CDCl_3)$ 15.8 (q), 17.1 (q), 17.7 (s), 23.3 (t), 27.6 (q), 27.6 (t), 27.6 (t), 29.2 (d), 33.6 (d), 40.6 (t), 67.3 (t), 123.7 (d), 126.0 (d), 134.4 (s), 139.0 (s).
4: $\nu(CCl_4)$ 3060, 1635, 1390, 1380, 1220, 890 cm^{-1} ; $\delta(CDCl_3)$ 0.79, 1.04 (each 3H, s), 1.66 (3H, d, $J=1.5$ Hz), 4.83 (2H, br.s), 5.28 (1H, m).
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