

(-)-Myltaylenol, a Tricyclic Sesquiterpene Alcohol with a Novel Carbon Skeleton from the Liverwort *Mylia taylorii*

Daisuke Takaoka,^a Akihiko Matsuo,^{*b} Junji Kuramoto,^b Mitsuru Nakayama,^b and Shûichi Hayashi^c

^a Department of Chemistry, Faculty of General Education, Ehime University, Matsuyama 790, Japan

^b Department of Chemistry, Faculty of Science, Hiroshima University, Naka-ku, Hiroshima 730, Japan

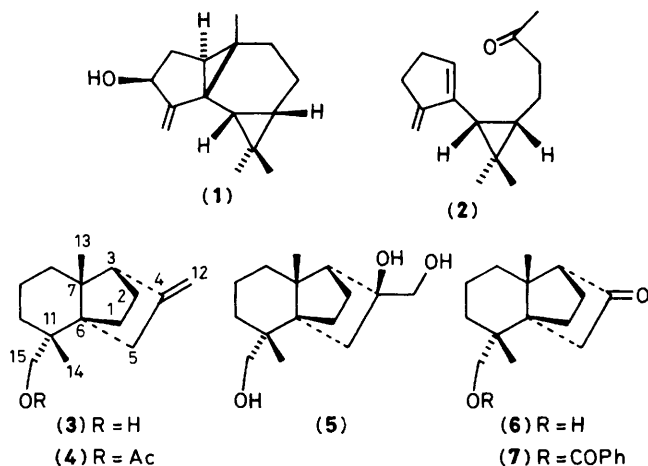
^c Department of Chemistry, Faculty of Science, Okayama University of Science, Okayama 700, Japan

A sesquiterpene alcohol (-)-myltaylenol with a novel carbon skeleton has been isolated from the liverwort *Mylia taylorii*, and its structure (**3**), including the absolute configuration, has been determined on the basis of chemical and spectroscopic evidence as well as X-ray analysis of the benzoate derivative (**7**).

We have already reported^{1,2} the isolation and structure determination of the two sesquiterpenoids (-)-myliol (**1**) and (-)-taylorione (**2**), both with novel carbon skeletons, from the liverwort *Mylia taylorii* (Hook.) S. Gray. We have now obtained a third sesquiterpenoid, (-)-myltaylenol, from the same liverwort and have determined its structure (**3**) and

absolute stereochemical configuration; it possesses a novel irregular sesquiterpene skeleton.[†]

[†] We suggest the trivial name myltaylane for the new skeleton, numbered as in (**3**) on the basis of the numbering of the presumed biogenetic precursor *cis*-farnesyl pyrophosphate. Thus, (-)-myltaylenol is myltayl-4(12)-en-15-ol.



(-)-Myltaylenol (**3**), C₁₅H₂₄O, m.p. 69–70.5 °C, [α]_D -59°, was isolated as a minor constituent of the ethanol extract of the liverwort in 0.35% yield. Its spectroscopic properties showed that it was a tricyclic sesquiterpenoid containing a primary hydroxy [ν 3325 and 1035 cm⁻¹; δ_{H} 3.12 and 3.42 (each 1H, d, J 10.0 Hz); δ_{C} 77.2 (t)], an exomethylene [ν 1740, 1662, and 870 cm⁻¹; δ_{H} 4.50 and 4.70 (each 1H, br.s); δ_{C} 154.1 (s) and 101.7 (t)], and two tertiary methyl groups [δ_{H} 1.02 and 1.05 (each 3H, s); δ_{C} 19.3 and 17.5 (each q)].[‡] Other features of the ¹³C n.m.r. spectrum showed six methylene [δ_{C} 39.6, 30.9, 30.0, 29.2, 28.0, and 18.3 (each t)], one methine [δ_{C} 56.9 (d)], and three quaternary carbon atoms [δ_{C} 51.2, 47.5, and 38.6 (each s)]. The presence of the primary hydroxy group was confirmed by formation of the acetate (**4**), C₁₇H₂₆O₂, [α]_D -38° [ν 1740 and 1240 cm⁻¹; δ_{H} 2.02 (3H, s) and 3.68 and 3.85 (each 1H, d, J 10.0 Hz)]. Oxidation of (**3**) with OsO₄ produced the triol (**5**), C₁₅H₂₆O₃, m.p. 111.5–112.5 °C, [α]_D -46° [ν 3250 and 1030 cm⁻¹; δ_{H} 3.10 and 3.38 (each 1H, d, J 10.0 Hz) and 3.65 (2H, s)] which was then converted into the nor-ketone (**6**), C₁₄H₂₂O₂, m.p. 202–203 °C, [α]_D +36° [ν 3500 and 1720 cm⁻¹; δ_{H} 3.13 and 3.38 (each 1H, d, J 10.0 Hz)] by NaIO₄ oxidation.

Because of the limited availability of compound (**3**) for structural correlation with any known sesquiterpenoid, an X-ray crystallographic study was carried out. The benzoate (**7**), C₂₁H₂₆O₃, m.p. 159 °C, [α]_D +36° [ν 1740 and 1715 cm⁻¹], derived from the keto-alcohol (**6**), afforded suitable crystals.

Crystal data: C₂₁H₂₆O₃, $M = 326.4$, orthorhombic, space group $P2_12_12_1$, $a = 8.203(1)$, $b = 9.840(1)$, $c = 21.238(3)$ Å, $U = 1714.3$ Å³, $D_c = 1.26$ g cm⁻³, $Z = 4$, $F(000) = 704$, $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, $\mu = 0.9$ cm⁻¹.

The diffraction intensities with $2\theta \leq 55^\circ$ were collected in the variable speed ω scan mode with graphite-monochromated Mo-K α radiation on a Syntex R3 four-circle diffractometer. Of 2269 independent reflections, 1836 having $F_o \geq 3\sigma(F_o)$ were judged to be observed after correction for Lorentz, polarization, and background effects. The structure was solved by direct methods (MULTAN 78),³ and refine-

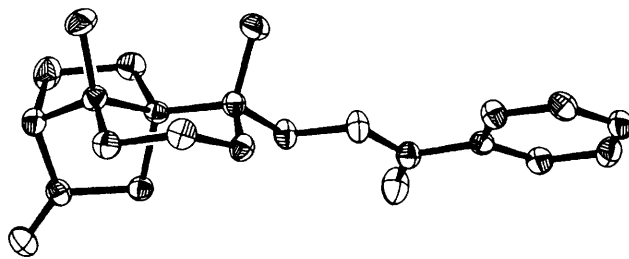


Figure 1. X-Ray structure of the benzoate (**7**).

ment by full-matrix least-squares using anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for the hydrogen atoms with the UNICS III program system⁴ led to a final R -value of 0.048.[§] The structure of the nor-ketobenzoate (**7**) thus determined is shown in Figure 1. The molecule consists of a norbornane fused to a cyclohexane ring. The absolute configuration was established by analysis of the c.d. spectrum [$\lambda(\text{MeOH})$ 291 nm ($\Delta\epsilon + 2.08$)] of the norbornan-2-one derivative (**6**) to be as shown in this structure.⁵

Accordingly, the structure and absolute configuration of (-)-myltaylenol are as shown in structure (**3**) having a novel sesquiterpene skeleton; this does not conform to the isoprene rule⁶ for 1,2-methyl migration. The myltaylene framework may be derived from *cis*-farnesyl pyrophosphate through C-3, C-7 cyclization of β -chamigrene followed by migration of the C-3 methyl group to the vicinal position, since sesquiterpenoids having a similar framework: 3,13-cyclochamigrane or rhodolaurane, have been isolated from the genus *Laurencia*⁷ and the carbon skeleton has been correlated chemically with a halogenated β -chamigrene of known structure.⁷

We thank Dr. Kaoru Kuriyama, Shionogi Research Laboratory, for c.d. spectra.

Received, 31st December 1984; Com. 1799

References

- V. Benešová, P. Sedmera, V. Herout, and F. Šorm, *Tetrahedron Lett.*, 1971, 2679; A. Matsuo, H. Nozaki, M. Nakayama, Y. Kushi, S. Hayashi, N. Kamijo, V. Benešová, and V. Herout, *J. Chem. Soc., Chem. Commun.*, 1976, 1006.
- A. Matsuo, S. Sato, M. Nakayama, and S. Hayashi, *Tetrahedron Lett.*, 1974, 4219; *J. Chem. Soc., Perkin Trans. 1*, 1979, 2652.
- P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declereq, and M. M. Woolfson, MULTAN 78, University of York, 1978.
- T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, 1979, 55, 69.
- D. N. Kirk, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2122.
- L. Ruzicka, *Proc. Chem. Soc., London*, 1959, 341.
- A. G. González, J. D. Martín, V. S. Martín, M. Norte, and R. Pérez, *Tetrahedron Lett.*, 1982, 23, 2395.

[‡] I.r. and n.m.r. spectra, respectively, were determined for KBr pellets and CDCl₃ solutions, and optical rotations for CHCl₃ solutions. All new compounds (**3**)–(**7**) gave spectral data in good agreement with the assigned structures.

[§] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.