

TRITERPENE FROM *LIMNOPHILA HETEROPHYLLA*

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Key Word Index—*Limnophila heterophylla*; Scrophulariaceae; methyl-olean-12-ene-3 α -benzoyloxy-29-carboxylate.**Abstract**—The petrol extract of the aerial parts and roots of *Limnophila heterophylla* yielded a new triterpene, methyl-olean-12-ene-3 α -benzoyloxy-29-carboxylate.

In the course of our studies on plant pigments, a systematic phytochemical investigation of *Limnophila heterophylla* (Roth) Merrill. [1] has been undertaken. In this paper we report the isolation and characterization of a new pentacyclic triterpene, methyl-olean-12-ene-3 α -benzoyloxy-29-carboxylate (1) from the petrol (60–80°) extract of the whole plant of *L. heterophylla*.

3 α -Benzoyloxy-methyl katonate (1), C₃₈H₅₄O₄ ([M]⁺ at *m/z* 574), gave a positive Liebermann–Burchardt test for a pentacyclic triterpene. Its IR spectrum showed absorption bands at $\nu_{\text{max}}^{\text{KBr}}$ cm^{−1}: 1700 (ester carbonyl) and 1645, 1600, 1580, 1500 (aromatic unsaturation). The ¹H NMR spectrum of the triterpene displayed signals for (i) seven tertiary methyls at δ 0.75 (3H, s), 0.88 (6H, s), 0.96 (9H, s) and 1.25 (3H, s); (ii) one proton multiplet at δ 5.50 assignable to >CH–O–C(O)–C₆H₅; (iii) a three proton singlet at δ 3.50 for a carbomethoxy function; (iv) one vinylic proton at δ 5.25 (1H, m); and (v) five aromatic protons at δ 7.60 (3H, m) and 7.80 (2H, m),

indicating the presence of a monosubstituted benzene ring in the triterpene.

The mass spectrum of this triterpene was similar to the Δ^{12} -oleanene type of pentacyclic triterpene [2] and gave peaks at *m/z* 574 [M]⁺, 559 [M – Me]⁺, 452 [M – C₆H₅CO₂H]⁺, 262 (retro-Diels–Alder fragmentation, around ring C), 311 [M – 262 – H]⁺, 247 [262 – Me], 202 [262 – MeO₂CH] and 189 [311 – C₆H₅CO₂H]. Furthermore, from mass values of the above peaks it is evident that the carboxymethyl group is in the D/E ring portions, while the benzoyloxy group is present in the A/B ring portions and its location at C-3 is highly probable from a biogenetic background. Finally, hydrolysis of this triterpene to benzoic acid and katonic acid (2), 3 α -hydroxy-olean-12-ene-29-oic acid [3], led us to formulate this triterpene as methyl-olean-12-ene-3 α -benzoyloxy-29-carboxylate (1).

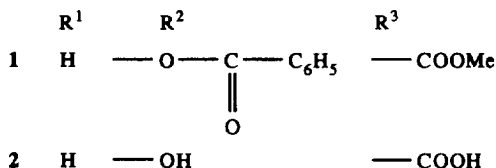
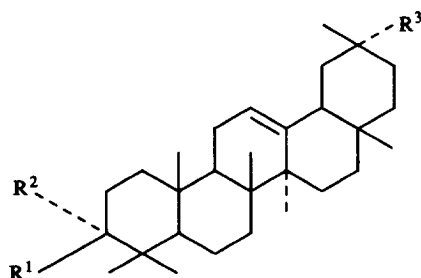
EXPERIMENTAL

All mps: uncorr. Whole plants of *Limnophila heterophylla* were collected from Santiniketan and their identity verified by Dr H. R. Chowdhury and Dr P. K. Dan (Visva-Bharati University). A specimen of the plant is preserved in the Natural Products Laboratory of this University.

Extraction of *L. heterophylla*. Air-dried defatted powdered whole plants (1.5 kg) of *L. heterophylla* were extracted with petrol (60–80°) in a Soxhlet apparatus for 56 hr. The extract was concd under red. pres. and then subjected to CC on 200 g silica gel (60–120 mesh).

Isolation of triterpene (1). The C₆H₆ eluent afforded methyl-olean-12-ene-3 α -benzoyloxy-29-carboxylate (yield 0.5 g), mp 210–212°; UV, IR, ¹H NMR (90 MHz, CDCl₃) and mass spectral data are described in the text.

Hydrolysis of triterpene (1). The triterpene (1) (0.2 g) was refluxed with 20% ethanolic KOH (10 ml) for 8 hr, the solvent removed, H₂O added and the mixt. filtered.



The filtrate was acidified with dilute HCl and cooled, when needles of benzoic acid (0.05 g), mp 120–122° sepd out. The aq. layer was extracted with Et₂O, washed with H₂O, dried and the solvent removed. The residue on repeated CC over silica gel (50 g) furnished kationic acid (2) (0.05 g), C₃₀H₄₈O₃, [M]⁺ *m/z* 456, mp 280–282°, ν_{\max}^{KBr} cm⁻¹: 3450 (–OH), 1690 (–CO₂H) and 1650 (unsatn); methyl ester, C₃₁H₅₀O₃, [M]⁺ *m/z* 470, mp 190°; ester-acetate, C₃₃H₅₂O₄, [M]⁺ *m/z* 512, mp 199–200°.

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