

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) Merill. [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**), $C_{38}H_{54}O_4$ ($[M]^+$ at m/z 574), gave a positive Liebermann–Burchardt test for a pentacyclic triterpene. Its IR spectrum showed absorption bands at $\nu_{\text{max}}^{\text{KBr}} \text{ cm}^{-1}$: 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 $>\text{CH}-\text{O}-\text{C}(\text{O})-\text{C}_6\text{H}_5$; (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 $[M - \text{Me}]^+$, 452 $[M - \text{C}_6\text{H}_5\text{CO}_2\text{H}]^+$, 262 (retro-Diels–Alder fragmentation, around ring C), 311 $[M - 262 - \text{H}]^+$, 247 $[262 - \text{Me}]$, 202 $[262 - \text{MeO}_2\text{CH}]$ and 189 $[311 - \text{C}_6\text{H}_5\text{CO}_2\text{H}]$. 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**).

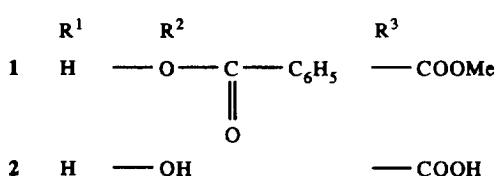
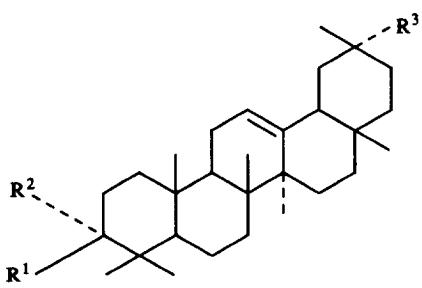
EXPERIMENTAL

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 C_6H_6 eluent afforded methyl-olean-12-ene-3 α -benzoyloxy-29-carboxylate (yield 0.5 g), mp 210–212°; UV, IR, ^1H NMR (90 MHz, CDCl_3) 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, H_2O 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 Et_2O , washed with H_2O , dried and the solvent removed. The residue on repeated CC over silica gel (50 g) furnished katonic acid (2) (0.05 g), $\text{C}_{30}\text{H}_{48}\text{O}_3$, $[\text{M}]^+$ m/z 456, mp 280–282°, $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3450 (–OH), 1690 (–CO₂H) and 1650 (unsatn); methyl ester, $\text{C}_{31}\text{H}_{50}\text{O}_3$, $[\text{M}]^+$ m/z 470, mp 190°; ester-acetate, $\text{C}_{33}\text{H}_{52}\text{O}_4$, $[\text{M}]^+$ m/z 512, mp 199–200°.

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