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DITERPENOID QUINONES OF *SALVIA LANATA**

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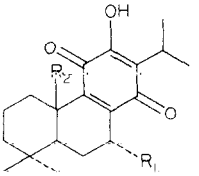
Key Word Index—*Salvia lanata*, Labiatae, 20-hydroxy-7α-acetoxyroyleanone, royleanone

Abstract—Two diterpenoid quinones, 20-hydroxy-7α-acetoxyroyleanone and royleanone, have been isolated from the whole plant (aerial parts and roots) of *Salvia lanata*

In our previous communications [1, 2], we reported the isolation of three diterpenoid quinones, horminone, desacylnemorone and 7α-acetoxyroyleanone, and a new pentacyclic triterpenic acid, 3-epi-ursolic acid, from the petrol extract of the whole plant (aerial parts and roots) of *Salvia lanata* Roxb. In this communication we report the isolation of two more diterpenoids having an abietane skeleton from the benzene extract of the plant. One of them is royleanone whilst the other appears to be a new quinone, the structure of which has been elucidated as 20-hydroxy-7α-acetoxyroyleanone (**1**) on the basis of chemical and spectral studies.

20-Hydroxy-7α-acetoxyroyleanone, $C_{22}H_{30}O_6$ (M^+, *m/z* 390), mp 160–162°, exhibits UV λ_{max}^{MeOH} nm(ε): 280 (12 000) and 407 (600). Its IR spectrum shows the presence of acetyl, hydrogen bonded hydroxyl and α,β-unsaturated carbonyl groups. Its ^{1}H NMR spectrum ($CDCl_3$, 100 MHz) is strikingly similar to that of 7α-acetoxyroyleanone (**3**) [3–5] but lacks the angular methyl proton signal at δ1.30. Instead, it shows a peak at δ 3.58 (2H, *d*, *J* = 10 Hz) indicating the presence of a $-CH_2OH$ group. The presence of two intense peaks at *m/z* 359 $[M-CH_2OH]^+$ and 344 $[M-CH_2OH\text{-}Me]^+$ in the mass spectrum of the compound also supports the above view. Further evidence in favour of the structure **1** for the diterpenoid is provided by the nature of the unsaponifiable product of this compound. Thus, saponification of **1** gave rise to **2**, $C_{20}H_{28}O_5$, mp 165–168°, the ^{1}H NMR spectrum ($CDCl_3$, 100 MHz) of which, as expected, is practically identical to that of horminone (**4**) [1, 4, 5], except for the absence of an angular methyl proton signal. Instead, it has a doublet (2H, *J* = 10 Hz) around δ 3.64 for a $-CH_2OH$ group. All these spectral and chemical observations reveal that the diterpenoid differs from 7α-acetoxyroyleanone (**3**) by replacement of the methyl group at C-10 with a hydroxymethyl group. Its structure is, therefore, 20-hydroxy-7α-acetoxyroyleanone (**1**).



1 R_1 = OAc, R_2 = CH_2OH
2 R_1 = OH, R_2 = CH_2OH
3 R_1 = OAc, R_2 = Me
4 R_1 = OH, R_2 = Me

EXPERIMENTAL

All mps are uncorr.

Isolation of royleanone and **1**. Ca 1 kg of defatted plant material was extracted with C_6H_6 in a Soxhlet for 45 hr. The extract was subjected to CC on 200 g Si gel (mesh 60–120). The petrol (60–80°)–C_6H_6 (1:1) eluate yielded royleanone which was crystallized from MeOH as yellow plates $C_{20}H_{28}O_3$ (M^+, *m/z* 316), mp 182°, yield 0.08 g. Its spectral data were similar to those reported in the lit. [3].

The fraction eluted with C_6H_6 gave 20-hydroxy-7α-acetoxyroyleanone. It crystallized as brown plates from $CHCl_3$–*n*-hexane (1:3), yield 0.4 g, mp 160–162°. UV λ_{max}^{MeOH} nm (ε): 280 (12 000) and 407 (600). IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1735, 1665 and 1625. ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 0.90 (6H, s, 2 × Me), 1.10 and 1.15 (6H, *d*, *J* = 6 Hz, $-CHMe_2$), 2.05 (3H, s, OOC Me), 3.25 (1H, *septet*, *J* = 7 Hz, $CHMe_2$), 3.60 (2H, *d*, *J* = 10 Hz, $-CH_2OH$), 5.70 (1H, *br*, $W_{\frac{1}{2}}$ = 8 Hz, CH–O–CO–Me) and 7.20 (1H, *br* s, phenolic-OH).

Saponification of **1**. 20-Hydroxy-7α-acetoxyroyleanone (**1**, 0.03 g) in MeOH (5 ml) was refluxed for 4 hr with 10 ml 10% methanolic KOH. The saponification mixture was then cooled, filtered, acidified with dil. HCl and extracted with $CHCl_3$. The $CHCl_3$ extract was then washed with H_2O, dried over Na_2SO_4 and the solvent removed. On repeated CC over Si gel (50 g) the residue furnished **2**. $C_{20}H_{28}O_5$, mp 165–168°. IR ν_{max}^{KBr} cm^{-1}: 3510, 3340, 1665 and 1625. ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 0.90 (6H, s, 2 × Me), 1.10 and 1.15 (6H, *d*, *J* = 6 Hz, $-CHMe_2$), 3.25 (1H, *septet*, *J* = 7 Hz, $-CHMe_2$), 3.64 (2H, *d*, *J* = 10 Hz, CH_2OH), 4.75 (1H, *br* s, $W_{\frac{1}{2}}$ 8 Hz, CHOH) and 7.20 (1H, *br* s, phenolic-OH).

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* Part 2 in the series "Diterpenoid Quinones of *Salvia lanata*". For Part 1 see ref. [1].

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LIMONOID EXTRACTIVES FROM *XYLOCARPUS MOLUCCENSIS*

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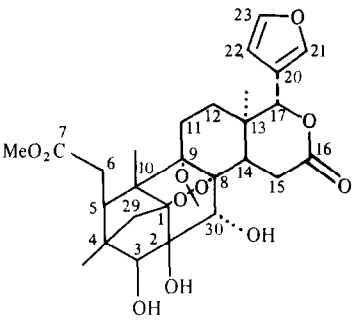
Key Word Index—*Xylocarpus moluccensis*, Meliaceae; limonoids; phragmalin, xyloccensin G, xyloccensin H

Abstract—Further examination of the timber of *Xylocarpus moluccensis* has given three new compounds, xyloccensins G, H and I. Structures are deduced for G and H. A structure is also deduced for xyloccensin C and proposals are made concerning the biosynthesis of phragmalin

The outstanding problem in the phytochemistry of the limonoids is how the ring A bridge is formed in the 1,29-cycloswietenan group of compounds, of which phragmalin (**1**) is the simplest known example. So far the only plant investigated containing cycloswietenans and simpler limonoids which appear possible as biosynthetic intermediates is *Xylocarpus moluccensis* [1], which has given phragmalin triacetate (xyloccensin E), a group of 1,8-



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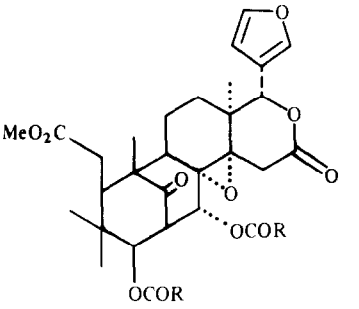

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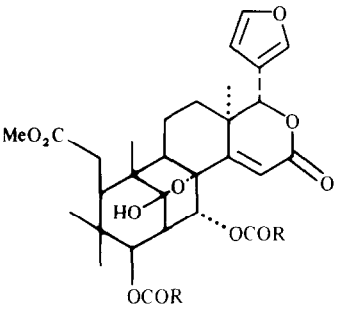

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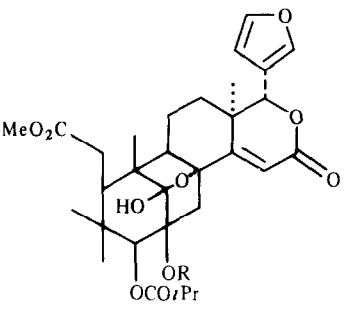

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