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SESQUITERPENE LACTONES OF *PODANTHUS MITIQUI*

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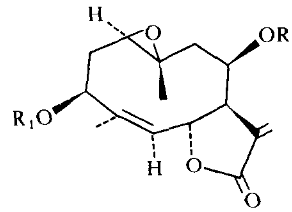
Key Word Index—*Podanthus mitiqui*; Compositae; sesquiterpene lactones; germacranolides.

Earlier work on stems and leaves of a cytotoxic plant, *Podanthus mitiqui* (Compositae) led to the isolation of three sesquiterpene lactones [1, 2]. A re-investigation of the stems and leaves of *Podanthus mitiqui* has now yielded two more compounds of this class.

The first compound **1**, $C_{24}H_{30}O_7$, has mp 155–158° and is hitherto unknown. Its mass spectrum shows a parent ion at m/z 340, consistent with the assigned formula, in addition to typical ions at m/z 361 (M^+ − methacrylyl), 347 (M^+ − angeloyl), 344 (M^+ − methacrylic acid), 278 (M^+ − angeloyl-methacrylyl), 261 (M^+ − methacrylic acid − angeloyl), 244 (M^+ − methacrylic acid − angelic acid). The IR spectrum exhibits the typical absorptions for an ester (1715 cm^{-1}) and α-methylene-γ-lactone groups (1762, 1660, 970 cm^{-1}). The UV absorption maximum at 212 nm (ε 30 784) supports the presence of the latter group.

The structural assignment of the sesquiterpene nucleus was largely based on ^{1}H NMR studies, extensive decoupling experiments and the use of europium induced shift experiments using Eu(fod)$_3$ reagent. The ^{1}H NMR parameters and structural assignment are given in the Experimental. The second compound **2** isolated from the plant was proved to be erioflorin methacrylate [3] by comparison with an authentic sample.



1 R_1, R_2 = CO—<; CO—C(Me)=C(Me)H

2 $R_1 = R_2$ = CO—<

EXPERIMENTAL

Material and isolation procedure. Plants were collected and extracted as before [1]. Fractionation of 300 g of methanolic extract over a Si gel column gave fractions which contained mixtures of **1** and **2**. Separation of these mixtures by high pressure liquid chromatography (HPLC) on Si-5 (hexane–*iso*-propanol) gave a small amount of each purified compound.

Compound **1**. Crystallized as colourless needles (8 mg), mp 157–158°; IR ν_{max}^{KBr} cm^{-1}: 2920, 2850, 1760, 1715, 1705, 1695, 1660, 1635, 1460, 1390, 1270, 1225, 1145, 1135, 970, 895; UV λ_{max}^{MeOH} nm: 212 (ε 30 784); ^{1}H NMR (CDCl$_3$ at 200 MHz): δ 2.64 (*dd*, *J* = 4, 10 Hz, H-1), 1.87 (*ddd*, *J* = 2, 10, 14.5 Hz, H-2α), 2.56 (*ddd*, *J* = 4, 5, 14.5 Hz, H-2β), 5.30 (*dd*, *J* = 2, 5 Hz, H-3), 5.33 (*dq*, *J* = 11, 1.5 Hz, H-5), 6.09 (*dd*, *J* = 2, 11 Hz, H-6), 2.9 (*m*, H-7), 5.22 (*m*, H-8), 2.83 (*dd*, *J* = 4.5, 15.5 Hz, H-9α), 1.37 (*dd*, *J* = 2, 15 Hz, H-9β), 1.46 (*s*, C-10, Me), 5.78 (*d*, *J* = 2 Hz, C-11=CH$_2$), 6.38 (*d*, *J* = 2 Hz, C-11=CH$_2$), 1.96 (*d*, *J* = 1.5 Hz, C-4 Me), 1.84 (*t*, *J* = 1.5 Hz, Me), 1.98 (*dm*, *J* = 7 Hz, Me), 2.00 (*d*, *J* = 1.5 Hz, Me), 5.62 (*t*, *J* = 1.5 Hz), 6.12 (*m*), 6.18 (*t*, *J* = 1.5 Hz). (The last six signals are for acyls.) MS m/z 430 (M^+), 361 (M^+ − methacrylyl), 347 (M^+ − angeloyl), 344 (M^+ − methacrylic acid), 278 (M^+ − angeloyl − methacrylyl), 261 (M^+ − methacrylic acid − angeloyl), 244 (M^+ − methacrylic acid − angelic acid), 83, 69, 55.

Erioflorin methacrylate **2**. Mp 155–158°; IR ν_{max}^{KBr}: cm^{-1} 1762, 1715, 1635, 1295, 1285, 1160, 1140, 985, 818, 715; ^{1}H NMR (CDCl$_3$ at 200 MHz): δ 1.37 (1 H, *dd*, *J* = 2, 15 Hz, H-9), 1.46 (3 H, *s*, C-10, Me), 1.88 (1 H, *m*, H-2), 1.96 (3 H, *d*, *J* = 1.5 Hz, C-4, Me), 2.68 (2 H, *m*, H-1, H-2), 2.9 (2 H, *m*, H-7 and H-9), 5.16 (1 H, *m*, H-8), 5.27 (1 H, *dd*, *J* = 2, 5 Hz, H-3), 5.33 (1 H, *m*, H-5), 5.82 (1 H, *d*, *J* = 2 Hz, H-13), 6.12 (1 H, *dd*, *J* = 2, 11 Hz, H-6), 6.38 (1 H, *d*, *J* = 2 Hz, H-13) and methacrylates (1.92, 2.0, 5.4, 5.64, 6.06); MS (m/z): 416 (M^+ very weak), 347 (M^+ − methacrylyl), 330 (M^+ − methacrylic acid), 261, 244 (M^+ − 2 methacrylic acid units), 83, 69, 55). By comparison of TLC and HPLC, as well as the spectra, this compound was proved to be identical with an authentic sample of erioflorin methacrylate.

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