Pergamon 0031-9422(95)00772-S

Phytochemistry, Vol. 41, No. 4, pp. 1105–1106, 1996

0031-9422/96 $15.00 + 0.00

A GERMACRANOLIDE FROM *ARTEMISIA PALLENS**

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(*Received in revised form* 30 *August* 1995)

Key Word Index—*Artemisia pallens*; Asteraceae; davana; sesquiterpene lactone; germacranolide.

Abstract—A new germacranolide has been isolated from the aerial parts of *Artemisia pallens* and the structure was established as 4,5β-epoxy-10α-hydroxy-1-en-3-one-*trans*-germacran-6α,12-olide by critical comparison with tagitinin C and spectral analysis.

INTRODUCTION

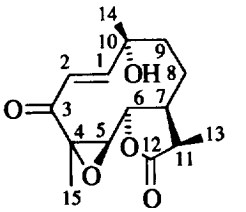
Artemisia pallens Walls ex DC., commonly known as Davana, is an aromatic herb found abundantly in damp situations in the plains all over India. The chemical composition of the oil from *A. pallens* has been investigated by a number of research groups [1–5]. Here, we report the isolation of a new compound (**1**), which is related to tagitinin C [6], from the extract of aerial parts of *A. pallens*.

RESULTS AND DISCUSSION

The acetone extract of *A. pallens* on repeated column chromatography coupled with preparative TLC gave compound **1** as a crystalline solid, mp 160–162°, molecular formula $C_{15}H_{20}O_5$, $[M]^+$ at *m/z* 280, which showed characteristic bands in its IR spectrum at 3480, 1785 and 1685 cm^{-1}, revealing the presence of hydroxyl, γ-lactone and a conjugated carbonyl.

In the ^1H NMR spectrum of **1**, the characteristic doublets of the exomethylene protons at C-13 of an α,β-unsaturated sesquiterpene-γ-lactone were not present, but instead there was a methyl group at δ1.23 (*d*, $J = 6.8$ Hz). The configuration of the methyl group was deduced from the coupling constant of H-11 (δ2.35 *dq*, $J = 6.8$ and 8.0 Hz). The presence of two methyl groups on oxygen-bearing carbon atoms was revealed by two singlets at δ1.20 and 1.50. Two signals of one proton each at δ5.85 (*d*, $J = 10$ Hz) and 6.60 (*d*, $J = 10$ Hz) in the ^1H NMR spectrum, and a signal at δ_C 201.8 in the ^{13}C NMR spectrum, were consistent with a conjugated enone system. The downfield shift of the C-10 methyl (δ1.50) suggested that the ketone could be at the C-3 position. The doublet of doublet nature of the C-6 lactonic proton appearing at δ 4.15 clearly indicated that the C-5 position was substituted with an oxygenated function and hence C-4/C-5 has an epoxide ring and the hydroxyl group is at C-10. The coupling constant (10, 12 Hz) of H-6 clearly showed the *trans*-lactone junction and H-5 as α-oriented. The presence of a secondary hydroxyl group was ruled out since the acetylation of **1** did not take place at room temperature.

Assignments of the protons were achieved by a ^1H–^1H homonuclear decoupling experiment. The ^{13}C NMR spectral data also agreed with the proposed structure (see Experimental). The compound **1** was thus identified as 4,5β-epoxy-10α-hydroxy-1-en-3-one-*trans*-germacran-6α,12-olide.



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EXPERIMENTAL

The IR spectrum was measured in $CHCl_3$, and ^1H NMR and ^{13}C NMR spectra in $CDCl_3$ with TMS as int. standard. The mass spectrum was recorded on a Finnigan Mat-1020, automated GC-MS. Optical rotation was performed on a JASCO-DIP-181 digital polarimeter. The UV spectrum was recorded on a Shimadzu-UV-240.

The shade-dried powdered plant material (1 kg), collected near Jejuri (Maharashtra, India) during December 1994, was extracted with Me_2CO. The Me_2CO extract (36 g), obtained as a thick viscous oil, was chromatographed over silica gel (200 g, 60–120 mesh) using Me_2CO–petrol with increasing proportions of Me_2CO as the elution gradient to provide 6 broad frs: A (12.0 g); B (7.0 g); C (3.2 g); D (4.5 g); E (2.0 g); F (6.0 g).

Fr. D (4.5 g) on repeated CC, together with prep. TLC with Me_2CO–petrol, yielded **1** (115 mg) as a crystalline solid.

*NCL Communication No. 6279.

Compound 1. Solid, mp 160–162°, $[\alpha]_D^{27}$ −19° (MeOH; *c* 0.14); UV λ_{max}^{MeOH} 217 (ε 6800) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3480, 1785, 1685; ^1H NMR (200 MHz): δ1.20 (3H, *s*, H-15), 1.50 *s* (3H, *s*, H-14), 1.23 (3H, *d*, *J* = 6.8 Hz, H-13), 1.65 (1H, *m*, H-7), 2.40 (1H, *d*, *J* = 10.0 Hz, H-5), 2.35 (1H, *dq*, *J* = 6.8, 8.0 Hz, H-11), 4.15 (1H, *dd*, *J* = 10.0, 12.0 Hz, H-6), 5.85 (1H, *d*, *J* = 10.0 Hz, H-2), 6.60 (1H, *d*, *J* = 10.0 Hz, H-1), 2.95 (1H, *br s*, OH). ^{13}C NMR (50.32 MHz): 152.0 (*d*, C-1), 125.7 (*d*, C-2), 201.8 (*s*, C-3), 46.4 (*s*, C-4), 54.7 (*d*, C-5), 79.7 (*d*, C-6), 40.7 (*d*, C-7), 22.8 (*t*, C-8), 34.3 (*t*, C-9), 70.2 (*s*, C-10), 52.5 (*d*, C-11), 178.4 (*s*, C-12), 19.9 (*q*, C-13), 23.9 (*q*, C-14), 12.6 (*q*, C-15); EIMS *m/z* (rel. int.): 280 $[M]^+$ (0.5), 262 (3), 247 (11), 201 (18), 173 (14), 98 (52), 69 (30), 55 (100).

Acknowledgement—The authors are grateful to the authorities of the Maharashtra Association of Cultivation of Science, Pune, India, for identification of the plant. A voucher specimen has been deposited in the National Chemical Laboratory herbarium.

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