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CAUDICIFOLIN, A NEW DITERPENE FROM *EUPHORBIA CAUDICIFOLIA*

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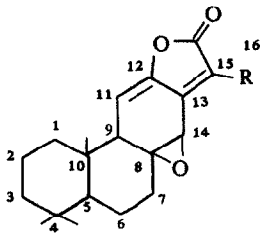
INTRODUCTION

Euphorbia caudicifolia L. Syn. *Euphorbia neriifolia* non L. (Euphorbiaceae) is found abundantly in the sandy terrain of Sind province in the South East of Pakistan. The latex and root extracts are used in the indigeneous system of medicine and are believed to possess antitumor properties [1]. This prompted us to investigate the alcoholic root bark extract which gave one new diterpenoid Caudicifolin (**1**) and the known diterpenoid [2, 3] Jolkinolide A (**2**) the structures of which are discussed below.



(**1**) R = CH_2OH
(**2**) R = Me
(**3**) R = CH_2OAc

RESULTS

The fresh root bark was extracted with ethanol at room temp. and the extract chromatographed on a Si gel column. Elution with $CHCl_3$–EtOAc (1:2) gave Caudicifolin (**1**) mp 177–182°. $C_{20}H_{26}O_4$: M^+ 330, requires C, 72.72; H, 7.87 found C, 73.16; H, 7.73% $[\alpha]_D^{25}$ = +94.4 (c = 0.7 $CHCl_3$). IR (KBr) cm^{-1}: 1738, (lactone C=O), 1648, 1667 (C=C), 3539 (OH). UV λ_{max}(MeOH) 288 nm (ε = 16 900). Proton NMR ($CDCl_3$ δ): 0.75, 0.88, 0.97 (9H, *s*, methyl 4,4,10), 4.06 (1H, *s*, CH-14), 4.67 (2H, *s*, CH_2-16), 5.59 (1H, *d*, *J* = 6Hz, CH-11), 2.67 (1H, *d*, *J* = 6Hz, CH-9). The signal of the hydroxyl proton was masked by CH-9 at 2.67. This was shown by the decrease in intensity of the doublet at 2.67 by addition of CF_3COOH. The IR of this compound also showed the presence of an OH group. This was confirmed when the treatment of this compound with Ac_2O and C_5H_5N gave the acetate (**3**). NMR ($CDCl_3$ δ): 0.72, 0.86, 0.95 (9H, *s*), 2.10 (3H, *s*, OAc), 3.95 (1H, *s*), 4.98 (2H, *s*), 2.69 (1H, *d*, *J* = 6 Hz), 5.62 (1H, *d*, *J* = 6 Hz). IR (film) cm^{-1}: 1648, 1752 (C=O).

Elution of the column with C_6H_6–$CHCl_3$ (1:1) gave a compound mp 220–225°. $C_{20}H_{26}O_3$: M^+ 314, UV λ_{max} MeOH 286 nm (ε 19 685). NMR ($CDCl_3$ δ): 0.73, 0.87, 0.96 (9H, *s*), 2.06 (3H, *s*), 2.63 (1H, *d*, *J* = 6Hz), 5.46 (1H, *d*, *J* = 6Hz), 3.72 (1H, *s*). The spectral data of this compound were identical when compared with the literature values of jolkinolide A (**2**).

The close similarity in the NMR spectrum of **1** and **2** clearly showed the presence of a hydroxymethylene group at C-15 in **1** instead of a methyl group as in **2**. That the conjugation pattern in **1** was identical with that in **2** was revealed by the comparison of UV spectra. Thus the OH group in **1** could only be placed at C-16. On the basis of above spectral data of Caudicifolin, its correlation with jolkinolide A from *Euphorbia jolkini* and the isolation of both natural products from the same source we assign structure **1** for Caudicifolin.

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