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A TERPENOID DIKETONE FROM THE LEAVES OF *PROSOPIS JULIFLORA*

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Key Word Index—*Prosopis juliflora*; Leguminosae; monocyclic diketone.

Abstract—A new monocyclic diketone, prosopidione, has been isolated from the leaves of *Prosopis juliflora*. Its structure was determined by spectral methods.

INTRODUCTION

Prosopis juliflora, a member of Mimosaceae family, is a shrub that grows abundantly in Sind and Punjab provinces of Pakistan [1]. Many plants of the genus *Prosopis* (Leguminosae) are known to have medicinal properties [2].

Siddiqui and Murthi [3] reported that the aqueous and alcoholic extract of this plant showed antibacterial activity. More recently Merzabani *et al.* [4] have reported the presence of a cytotoxic principle and patulitrin in the fruits of this plant, which exhibit significant activity against lung carcinoma. An extract of an allied species, *P. qlandulosa*, has recently been shown to be active against P-338, lymphocytic leukemia (Ps) and human epidermoid carcinoma of the nasopharynx (KB) [5]. In view of the therapeutic importance attributed to *P. juliflora*, comprehensive investigations on it have been carried out by various groups of workers [6, 7]. As a result of studies on dried leaves Ahmad and co-workers reported the isolation and structure elucidation of a number of new alkaloids [7, 8]. In this paper we wish to report the isolation and structure determination of a new diketone from this plant.

RESULTS AND DISCUSSION

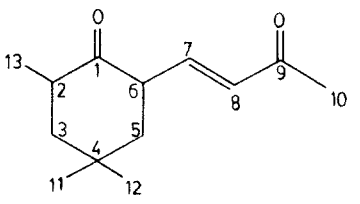
Prosopidione was isolated as a white amorphous powder, mp 202° (decomp.); $[\alpha]_D = -19.2°$ (MeOH; *c* 0.052). The EI and FD mass spectra showed a molecular ion peak at *m/z* 208. High resolution mass spectrometry gave the $[M]^+$ peak at *m/z* 208.14688 corresponding to the molecular formula $C_{13}H_{20}O_2$ (calc. 208.146321). An important fragment at *m/z* 165.127075 (calc. for $C_{11}H_{17}O$, 165.127935) was due to the loss of Ac from the molecular ion. Another fragment ion appeared at *m/z* 140.10736 with the composition of $C_9H_{16}O$ and was due to the loss of the side chain (2-ketobut-3-enyl) with proton transfer. The UV spectrum displayed maxima at 202 (log ε, 2.52) and 228 (log ε, 2.46) nm. The IR spectrum showed bands at 1710 (C=O), 1675 and 1650 (α,β-unsaturated ketone), 1260 (C–O stretching), 960 cm^{-1} (*trans*-olefin). The ^1H NMR spectrum in CD_3OD displayed signals due to four methyl groups at δ0.81 (*d*, *J* = 6.8 Hz, H-13), 0.87, 1.10 (2 × *s*, 2 × Me, H-11 and H-12) 2.26 (*s*, H-10), the last one due to Ac. There was a multiplet ascribed to H-2 at δ2.15 and a double doublet at δ1.7 (J_{gem} = 12.56 Hz, $J_{5\alpha,6}$ = 6.6 Hz, H-5α). The H-3 exhibited multiplet at δ1.5 (*m*, 2H-3). The doublets at δ6.33 (*J* = 16.04) and 6.88 (*J* = 16.04 Hz) are due to *trans*-olefinic protons at the C-7 and C-8 positions, respectively.

Two dimensional NMR measurements fully agreed with the proposed structure **1**. The 2D-*J*-resolved spectrum determined the multiplicities of the proton signals, while the coupling interactions were established by a COSY-45 experiment. The secondary methyl group showed a doublet at δ0.81 which was coupled with H-2 while the multiplet of H-2 at δ2.15 had cross peaks with the H-13 and H-3 protons. This technique indicated coupling of H-5 (δ1.7) with that of H-6 (δ4.5). These protons also show reciprocol NOE effects. The doublets at δ6.33 and 6.88 interacted with each other which was proved by NOE difference and homodecoupling technique. The proposed structure **1** is also confirmed by the ^{13}C NMR (75.43 MHz) spectrum which showed double bonded carbon signals at δ131.74 (C-7) and 153.96 (C-8). The signal of C-6 appeared downfield (δ75.76), due to the presence of a ketonic group and double bond at adjacent positions (C-1 and C-7). It also exhibited signals at δ200.84 (C-9), 182.64 (C-1) due to the carbonyl groups. Another quaternary carbon signal appeared at δ48.8 (C-4). The APT spectrum showed the presence of four methyl, two methylene, four methine and three quaternary carbons.

EXPERIMENTAL

Mp: uncorr. ^1H NMR (300 MHz) and ^{13}C NMR (75.43 MHz) spectra were recorded in CD_3OD using tetramethylsilane as an internal standard. Analytical TLC was carried out on a silica gel plates using the following solvent system $CHCl_3$–MeOH–NH_4OH (29:10:1).

Extraction and separation. The leaves of *Prosopis juliflora* (20 kg) were collected from the Karachi University and extracted exhaustively with MeOH. The residue obtained on evapn of the



methanolic extraction was partitioned between EtOAc and H_2O. The aq. layer was made alkaline with NH_3 (pH 9) and extracted repeatedly with $CHCl_3$. The alkaloid containing $CHCl_3$ layers were combined and evapd at red. pres. to afford a gummy residue, this was treated with C_6H_6 and the C_6H_6-soluble and C_6H_6-insoluble portions were obtained. The C_6H_6-soluble portion was selected for investigation and chromatographed on a neutral alumina column. The polar fractions were rechromatographed and yielded a colourless amorphous powder (12.2 mg).

Prosopidione. Mp 202° (decomp.); $[\alpha]_D = -19.2°$ (MeOH); UV λ_{max}^{MeOH} nm (log ε): 202 (2.46), 228 (2.52), IR ν_{max}^{KBr} cm^{-1}: 1675 (α,β-unsaturated ketone), 1260 (C–O), 960 (C–H) stretching for C=C. ^1H NMR (CD_3OD): δ 0.81 (*d*, *J* = 6.8 Hz, H-13), 0.87 (*s*, H-11), 1.10 (*s*, H-12), 2.26 (*s*, COMe), 2.15 (*m*, H-2), 1.7 (*dd*, J_{gem} = 12.56 Hz, $J_{5\alpha,6}$ = 6.6 Hz, H-5α), 1.8 (*dd*, J_{gem} = 12.52 Hz, $J_{5\beta,6}$ = 4.84 Hz, H-5β), 1.5 (*m*, 2H-3), 4.5 (*m*, H-6), 6.33 (*d*, *J* = 16.04 H-7) and 6.88 (*d*, *J* = 16.04 Hz, H-8).

HRMS. *m/z* 208.14688 (calc. for $C_{13}H_{20}O_2$ 208.146321), 165.127075 ($C_{11}H_{17}O$ 165.127935), 140.10736 ($C_9H_{16}O$. 140.120109), 125.13072 (C_9H_{17} 125.133019). ^{13}C NMR (CD_3OD, 75.43 MHz): δ 182.64 (C-1), 35.34 (C-2), 36.97 (C-3), 48.8 (C-4), 42.98 (C-5), 75.76 (C-6), 131.74 (C-7), 153.96 (C-8), 200.84 (C-9), 25.81 (C-10), 23.79 (C-11), 24.9 (C-12), 16.34 (C-13).

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ISOLATION OF THE 1α-HYDROXYCYCLOARTENOID MOLLIC ACID α-L-ARABINOSIDE FROM *COMBRETUM EDWARDSII* LEAVES

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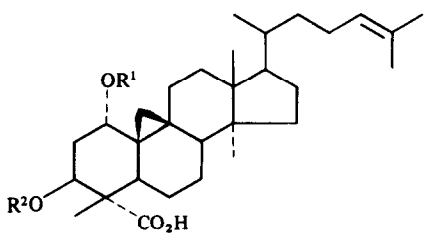
Key Word Index—*Combretum edwardsii*; Combretaceae; 1α-hydroxycycloartenoid arabinoside; ^{13}C NMR.

Abstract—The 1α-hydroxycycloartenoid glycoside, mollic acid 3-*O*-α-L-arabinopyranoside has been isolated from the leaves of *Combretum edwardsii*, revised ^{13}C NMR assignments for the aglycone mollic acid are given.

INTRODUCTION

The leaf extract of *C. edwardsii* has been found to be remarkably similar to that of *C. molle* in that they both contain mollic acid [**1**], and its arabinoside, glucoside and xyloside. However, whereas mollic acid β-D-glucoside is the major constituent and mollic acid α-L-arabinoside the minor constituent in *C. molle* [1, 2], the situation is reversed in *C. edwardsii*, which contains barely discernible quantities of the glucoside, but large quantities of the arabinoside and xyloside. No other *Combretum* species screened thus far have these four compounds [3], which suggests that these two species have a common ancestry despite now having marked differences in habitat and taxonomy; *C. edwardsii* is a climber restricted to a few forested areas of central and coastal Natal in South Africa, whereas *C. molle* is a medium sized tree distributed in a great variety of habitats throughout south, central and north-east Africa. The isolation of 9,19-cycloartenoids from yet another *Combretum* species also suggests that at some stage in the development of this genus a chemotaxonomically significant bifurcation in triterpenoid synthesis occurred, resulting in certain species, *C. molle* [1], *C. edwardsii*, and *C. eleaegnoides* [4], producing these compounds and other species, *C. imberbe* [5], *C.*



1 $R^1 = R^2 = H$
2 $R^1 = H$, R^2 = L-Ara
2a R^1 = Ac, R^2 = L-Ara(Ac)$_3$
3 $R^1 = H$, R^2 = D-xyl