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TRITERPENOIDS AND CHALCONE FROM *SYZYGIUM SAMARANGENSE**

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Key Word Index—*Syzygium samarangense*; *Eugenia javanica*; Myrtaceae; triterpene methyl ester; chalcone; ursolic acid; jacoumaric acid; arjunolic acid.

Abstract—A new triterpene, methyl 3-epi-betulinate in its native form and 4′,6′-dihydroxy-2′-methoxy-3′,5′-dimethyl chalcone along with ursolic acid, jacoumaric acid and arjunolic acid have been isolated from the aerial parts of *Syzygium samarangense*.

INTRODUCTION

Syzygium samarangense (syn. *Eugenia javanica* Linn.) occurs in Andaman and Nicobar Islands, India. It is cultivated in many parts of India for its edible fruit [1]. The alcoholic extractive of the plant *Syzygium samarangense* exhibited immunostimulant activity in the general biological screening programme of CDRI. So far no significant work on this species is reported in the literature. Therefore, a detailed chemical investigation on this plant was undertaken.

RESULTS AND DISCUSSION

The chloroform fraction of the alcoholic extract of the aerial part of the plant on column chromatography over silica gel yielded five compounds.

Compound **1**, $C_{31}H_{50}O_3$, $([M]^+$ at m/z 470), was found to be a new triterpene ester (responded positive to the Liebermann–Burchardt test) identified as methyl 3-epi-betulinate (mp 220°, $[\alpha]_D^{25} - 10$, $CHCl_3$; c 0.192) on the basis of its mass fragmentation and NMR spectra. Compound **1**, on acetylation, gave a monoacetate **1a**, $C_{33}H_{52}O_4$ ($[M]^+$ at m/z 512, δ2.07, 3H, *s*, OCOMe). The low $W_{1/2}$ value (6.75 Hz) of the C-3 methine proton in the ^{1}H NMR spectra of **1** (δ3.38, 1H, *br s*, CHOH) and **1a** (δ4.60, 1H, *br s*, CHOAc) suggested that it had the β-configuration and the C-3 oxygen function, therefore, had the α-configuration. It was also observed in the ^{13}C spectrum of **1** that C-3 appeared upfield by about 3 ppm as compared to the corresponding carbon in methyl betulinate [2]. Finally, the confirmation of the compound **1** as methyl 3-epi-betulinate was achieved by converting it to betulin (**1c**, H-3 at δ3.21, *dd*, J = 11.0 and 5.5 Hz) [2] by first oxidizing **1** to the keto derivative **1b** followed by LAH reduction. Isolation of 3-epi-betulinic acid has been reported earlier and its methyl ester was also prepared [3] but to the best of our knowledge epi-betulinic acid methyl ester as such has not been reported previously from a natural source.

Another compound (**2**) isolated from the plant gave a characteristic olive-green colour reaction for chalcones with freshly prepared $FeCl_3$ [4]. The IR spectrum of the chalcone displayed absorption bands for a free hydroxyl as well as a H-bonded hydroxy group (3360 and 2960 cm^{-1}) and for α,β-unsaturated C=O (1620 cm^{-1}). Its ^{1}H NMR spectrum exhibited signals for a mono-substituted phenyl group at δ7.42 and 7.65, a *trans*-disubstituted double bond at δ7.87 and 8.00 (J_{AB} = 16.0 Hz), two benzylic methyl groups at δ2.17 and 2.20 and one aromatic methoxyl at δ3.70. Furthermore, two signals at δ13.62 and 5.37, respectively, which disappeared on D_2O shake were ascribed to two hydroxyl groups, one of which was strongly hydrogen bonded. The EI-mass spectrum of **2** showed $[M]^+$ at m/z 298 and a base peak of m/z 91. One of the fragments at m/z 166 was indicative of a highly substituted phenyl ring with two hydroxyl, two methyl and one methoxyl groups. Thus, from the above spectral data, it became clear that the chalcone had a 2′,4′,6′-trioxygenation pattern which could lead to either of the two possible structures 2′,6′-dihydroxy-4′-methoxy-3′,5′-dimethyl chalcone (**2a**) or 4′-6′-dihydroxy-2′-methoxy-3′,5′,-dimethyl chalcone (**2b**). However, the chalcone was assigned the structure **2b** on the basis of its NOE difference spectrum which showed that the irradiation of the signal at δ3.70 (OMe) resulted in the enhancement of only one of the C-methyl signals at δ2.20 and also one of the olefinic signals at δ8.00 (PhCH=CHCO). These observations suggested that the methoxyl group was in close proximity to only one of the C-methyls (3′) as well as a β-olefinic proton. The ^{13}C NMR spectrum of **2** (Table 1) showed the presence of carbon carrying one methoxyl and two hydroxyl groups with signals at δ162.1, 159.3 and 130.2, respectively [5, 6],

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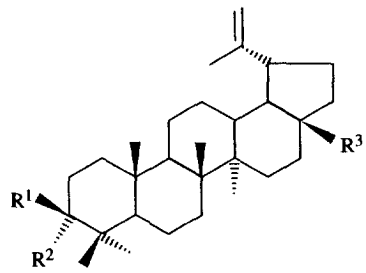

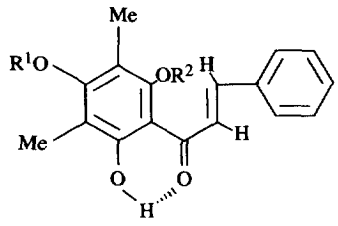

	R^1	R^2	R^3
1	H	OH	COOMe
1a	H	OAc	COOMe
1b	O	O	COOMe
1c	OH	H	CH_2OH

	R^1	R^2
2a	Me	H
2b	H	Me

Table 1. ^{13}C NMR spectral data for compound **2b** (100 MHz, $CDCl_3$)

C	2b
1	135.4
2	128.9
3	128.4
4	130.2
5	128.4
6	128.9
β	142.9
α	126.8
C=O	193.4
1′	106.6
2′	162.1
3′	108.9
4′	159.3
5′	109.1
6′	130.2
OMe	62.3
Me	8.2
Me	7.5

along with a low field signal at δ193.4 due to a chelated carbonyl carbon. Although the isolation of both the chalcones, **2a** and **b**, has already been reported [7, 8] from *Myrica gale*, the isolation of **2b** from *Syzygium samarangense* constitutes the second report from a natural source. The assignment of its ^{13}C NMR spectrum is reported for the first time.

Other triterpenoids isolated from this plant were identified as ursolic acid, jacoumaric acid and arjunolic acid (as the major constituent of the plant) by their spectral data (IR, EI-MS, ^1H and ^{13}C NMR) as well as by preparation of their acetates and methyl ester derivatives and comparing their spectral data with those reported in the literature [9–11].

EXPERIMENTAL

Plant material. Syzygium samarangense (aerial part) was collected from Chiriatapu (South Andaman, India). A voucher specimen of the plant is deposited in the herbarium of Botany Division, CDRI.

General. Mps: uncor.; IR: KBr; UV: MeOH, EtOAc; ^1H NMR: 400 MHz, TMS as int. standard; ^{13}C NMR: 100 MHz; EI-MS: direct inlet 70 eV; CC silica gel; TLC: silica gel coated plates using solvent systems (1) C_6H_6 (2) $CHCl_3$–MeOH (24:1), (23:2), (3) C_6H_6–MeOH (23:2). TLC chromatograms were visualized by spraying with 1% ceric sulphate in 1 M H_2SO_4 followed by heating at 110°.

Extraction. The alcoholic extractive (38 g) of the plant (aerial part 880 g) was resolved into *n*-C_6H_{14}, $CHCl_3$, *n*-BuOH and H_2O soluble fractions. The $CHCl_3$ soluble fraction (13 g) was chromatographed over silica gel. The column was eluted with *n*-C_6H_{14} and *n*-C_6H_{14}–EtOAc (19:1) in succession.

Isolation of methyl 3-epi-betulinate (**1**). The eluate *n*-C_6H_{14}–EtOAc (19:1) yielded compound **1** (20 mg) which was crystallized from *n*-C_6H_{14}–Me_2CO; mp 220°, $[\alpha]_D^{25}$ − 10° ($CHCl_3$: *c* 0.192). IR ν_{max}^{KBr} cm^{-1}: 3550, 1720. EI-MS *m/z*: 470 $[M]^+$, 452 $[M-18]^{+1}$, 411 $[M-CO_2Me]^+$, 262, 233, 220, 207, 203, 189. ^1H NMR: δ0.83, 0.85, 0.92, 0.93, 0.97, 1.68 (3H each, *s*, 6 × C-Me), 3.00 (1H, *dt*, *J* = 10.5, 4.2 Hz, H-19), 3.38 (1H, *br s*, $W_{1/2}$ = 6.8 Hz, CHOH), 3.68 (3H, *s*, OMe), 4.61 and 4.75 (1H each, *d*, *J* = 2.0 Hz, C=CH_2-29).

Isolation of chalcone **2**. Another *n*-C_6H_{14}–EtOAc (19:1) eluate of the gross chromatography furnished chalcone **2** (40 mg) which was crystallized from *n*-C_6H_{14}–Me_2CO; mp 120°; IR ν_{max}^{KBr} cm^{-1}: 3360, 2960, 2340, 1620, 1540, 1440, 1350, 1220, 1160, 1100, 970, 900, 810, 750, 680. UV λ_{max}^{MeOH} nm: 332.8 and 204.8; λ_{max}^{EtOAc} nm: 404.8, 303.2 and 212.0. EI-MS *m/z*: 298 $[M]^+$, 221 $[M-77]^+$, 206 $[M-92]^+$, 194 $[M-(Ph-CH=CH)-H]^+$, 166 $[194-CO]^+$, 165 $[194-HCO]^+$, 131 $[PhCH=CHCO]^+$, 103 $[PhCH=CH]^+$, 91 $[Ph-CH_2$ − base peak$]^+$, 77 [phenyl ring]: ^1H NMR: δ2.17 (3H, *s*,

C-Me), 2.20 (3H, *s*, C-Me), 3.70 (1H, *s*, OMe), 7.42 (3H, *m*), 7.65 (2H, *m*), 7.87 and 8.00 (1H each, *d*, AB-system, J_{AB} = 16.0 Hz), 5.37 and 13.62, (1H each, *s*, disappeared on D_2O shake). ^{13}C NMR: see Table 1.

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