Barbeyol: A New Phenolic Indane Type Component from *Barbeya oleoides*

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Barbeya oleoides, Barbeyol, Indane

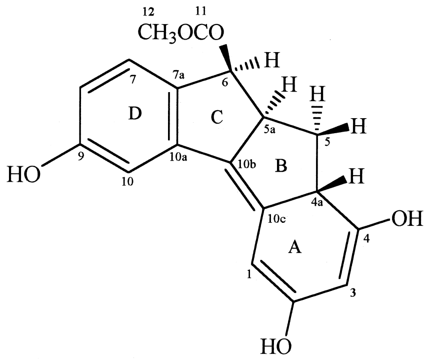
The aerial parts of *Barbeya oleoides* Schweinf (Family: Barbeyaceae) has afforded a new phenolic indane type component, which has been characterized as (6*R*, 4a*R*, 5a*R*)-5, 4a, 5a-trihydroindeno- (1, 2-a) indane-2, 4, 9-triol-6-O-β-acetate (**1**) on the basis of spectral analysis and has been designated as barbeyol.

Introduction

Barbeya oleoides Schweinf (Family: Barbeyaceae) locally known as *Kathah* in Arabic is widely distributed in tropical region including in Saudi Arabia (*Tanumah* and *Aseer* regions), Ethiopia, Somalia and Yemen (Chaudhury, 1998) and is used as folkloric remedy in the treatment of fever, infection, eden or related inflammatory diseases (Yesilada *et al.*, 1997). The literature survey revealed that no phytochemical work has been done so far on that plant. We report on a new indane-type phenolic component from the aerial parts of the plant, which has been characterized as (6*R*, 4a*R*, 5a*R*)-5, 4a, 5a- trihydroindeno- (1, 2-a) indane-2, 4, 9-triol-6-O-β-acetate (**1**) on the basis of spectral analysis and has been designated as barbeyol.

Results and Discussion

Compound **1** named as barbeyol was obtained as yellow-red viscous solid and had molecular composition $C_{18}H_{16}O_5$ as established on the basis of HRMS (M^+ 312.3244), elemental analysis, ^{13}C NMR and DEPT spectra. It gave a positive $FeCl_3$ test for phenols and exhibited absorption bands in IR spectrum at 3390 (OH), 1704 (C=O), 1610 (C=C), 1282 (C-O, ester linkage), 1140 (C-O, phenolic) and 1040 (C-O, alcoholic) cm^{-1}. The ^{13}C NMR and DEPT spectra showed 18 carbon atoms consisting of one methyl, one methylene, eight methines, seven quaternary carbon and one carbonyl carbon atom (in total $C_{18}H_{13}$) The sequential assignments of proton and carbon atoms were made with the help of ^1H-^1H COSY and ^1H-^{13}C COSY (HMQC) (Nakanishi, 1990) experiments starting with the easily distinguishable methylene and carbinyl protons at δ_H 2.368, 2.675 (δ_C 28.86) and 4.496 (δ_C 81.32) respectively, wherein the diastereotopic methylene protons exhibited correlations with each other as well as with H-5a and H-6 indicating the linkage of methylene group with carbinolic proton through a methine proton at position-5a. The carbinyl proton exhibited long-range couplings in HMBC spectrum (Nakanishi, 1990) with C-5, C-5a, C-10b, C-7 and C-8, which could place it at position-6 (Fig. 1) (Table I). Further, the ^1H- and ^{13}C NMR spectra displayed a three-proton singlet at δ_H 1.772 (CH_3, aliphatic), δ_C 172.07 (C=O) and 28.81 (CH_3) indicating an acetyl moiety in the molecule attributable at position-6. The cou-



Barbeyol (**1**)

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Table I. 1D-and 2-D NMR data of barbeyol (**1**).

Positions	^{1}H-NMR	^{13}C-NMR	DEPT**	^{1}H-^{1}H COSY Correlations	HMQC***		HMBC****
						$^2J_{CH}$	$^3J_{CH}$
1.	5.899 *d* (2.0)	95.48	CH	H-3	95.48 *d*	C-2, C-10c	C-3
2.	– –	156.79	C	– –	156.79 *s*	– –	– –
3.	5.702 *d* (2.0)	94.21	CH	H-1	94.21 *d*	C-4, C-10c	C-1
4.	– –	156.25	C	– –	156.25 *s*	– –	– –
4a.	1.239 *d* (1.5)	29.34	CH	– –	29.34 *d*	H-5	– –
5α*.	2.675 *dd* (5.0, 5.0)	28.18	CH_2	H-5ß, H-5a, H-6	28.18 *t*	C-5a	C-6, C-4, C-10c
5ß*.	2.368 *dd* (8.5, 8.0)	–do–	–do–	H-5α, H-5a, H-6	–do–	C-5a	C-6, C-4, C-10c
5a.	3.833 *dd* (7.5, 7.5)	66.66	CH	H-6, H-5ß, H-5α	66.66 *d*	– –	– –
6.	4.496 *d* (7.5, axial, α)	81.32	CH	H-5a, H-5ß, H-5α	81.32 *d*	C-5a	C-10b, C-5, C-7, C-8
7a.	– –	145.20	C	– –	145.20 *s*	– –	– –
7.	6.687 *d* (8.0)	115.43	CH	H-8, H-10	115.43 *d*	C-8	C-6
8.	6.596 *q* (2.0, 8.0)	118.77	CH	H-7, H-10	118.77 *d*	C-7	C-7a, C-10
9.	– –	155.69	C	– –	155.69 *s*	– –	– –
10.	6.735 *d* (3.5)	114.87	CH	H-8, H-7	114.87 *d*	C-10a	C-8, C-10b
10a.	– –	145.19	C	– –	145.19 *s*	– –	– –
10b.	– –	130.94	C	– –	130.94 *s*	– –	– –
10c.	– –	99.42	C	– –	99.42 *s*	– –	– –
11.	– –	172.07	C	– –	172.07 *s*	– –	– –
12.	1.772 *s*	22.81	CH_3	– –	22.81 *q*	C-11	– –
O*H*	4.888 *d* (7.0)	– –	– –	– –	– –	– –	– –
O*H*	7.309 *brs*	– –	– –	– –	– –	– –	– –

* Assignments were based on ^{1}H-^{1}H- and ^{1}H-^{13}C-COSY, and HMQC experiments; coupling constants in Hertz are given in parentheses; *s*: singlet, *d*: doublet, *m*: multiplet, *t*: triplet, *brs*: broad singlet. Methylene diastereotopic protons exhibited different δ_H in ^{1}H-NMR and same δ_C , but different signals in ^{13}C-NMR.
** DEPT chemical shifts are presented at $\theta = 3\pi/4$ when methylene groups reaches negative maximum.
*** C-multiplicities were established by DEPT experiment.
**** The correlations in HMBC have been shown from protons to carbons.

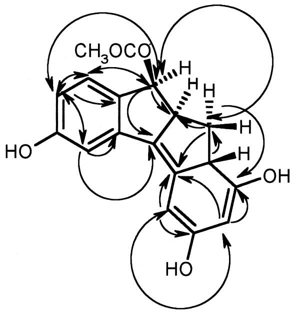


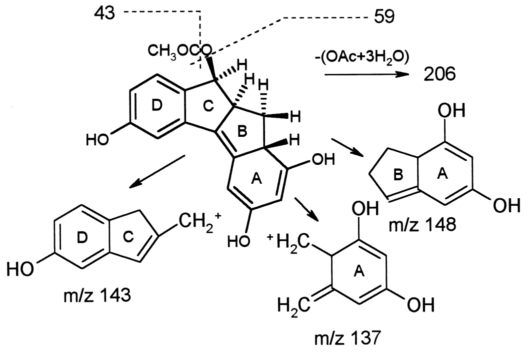
Fig. 1. Significant heteronuclear mujltiple bond correlations (HMBC) for barbeyol **1**. Arrows point fromt proton to carbon.

pling constant ($J = 7.5$ Hz) of the carbinolic proton at position-6 indicated the axial-axial coupling with H-5a, which confirmed the α-orientation of H-6, β-orientation of acetyl moiety and α-orientation of H-5a (Silverstein *et al.*, 1981). The signals at δ_H 1.239 (1H, *d*, $J = 1.5$ Hz), δ_C 29.34 due to H-4a showed correlation in HMBC spectrum with C-5, which allowed to place it at position-4a. The coupling constant ($J = 1.5$ Hz) indicated the equatorial-equatorial coupling with H-5 (equatorial) indicating the β-orientation of proton at position-4a (Silverstein *et al.*, 1981). Thus the configuration of rings-A, B and C could be established as 6*R*, 4a*R* and 5a*R* on the basis of above stereochemical studies.

The ^{1}H-and ^{13}C NMR spectra displayed signals at δ_H 5.899 (1H, *d*, J = 2.0 Hz), δ_C 95.48 and δ_H 5.702 (1H, *d*, J = 2.0 Hz), δ_C 94.21 indicating the presence of two olefinic protons in the molecule assignable at positions-1 and 3 of the ring-A on the basis of long-range couplings in HMBC spectrum, which displayed correlations with each other, C-10c, C-4 and C-2 (Fig. 1) (Table I). The signals at δ_H 6.687 (1H, *d*, J = 8.0 Hz, H-7), δ_C 115. 43; 6.596 (1H, *q*, J = 2.0, 8.0 Hz, H-8), 118.77 and 6.735 (1H, *d*, J = 3.5 Hz, H-10), 114.87 attributable for aromatic protons indicated the presence of an aromatic ring in the molecule. The H-7 and H-8 protons showed long-range couplings in HMBC spectrum with each other, C-6, C-7a and C-10 confirming their proposed positions in ring-D. The H-10 also displayed long-range couplings with C-8 and C-10a of ring-D and C-10b of ring-C indicating the proposed positions of rings-D, C and B (Table I) (Fig. 1). The signals at δ_C 130.90 and 99.42 attributable to olefinic quaternary carbon atoms could be placed at $\Delta^{10b(10c)}$ of the ring-B on the basis of long-range correlations in HMBC spectrum, wherein C-10b correlated with H-10 and H-6; and C-10c with H-5, H-1 and H-3. The ^{13}C NMR spectrum displayed three signals at δ_C 156.79, 156.25 and 155.69 indicating the presence of three phenolic/ enolic hydroxyl groups, substantiating further by a broad signal at δ 2.298 (9H, $3 \times$ OAc) in ^{1}H NMR spectrum of its acetate, which could be placed at positions-2, 4 and 9 respectively on the basis of long-range couplings in HMBC spectrum (Table I) (Fig. 1).

The mass spectrum of the compound also supported the proposed structure exhibiting prominent peaks at *m/z* 59 and 43 due to elimination of acetyl group, 206 due to elimination of three hydroxyl and one-acetoxyl groups, 148 due to elimination of ring-C and D, 137 due to rupture of ring-B, and 143 due to elimination of rings-A and B (Scheme 1).

Thus on the basis of above spectral analysis the structure of compound **1** was established as (6*R*, 4a*R*, 5a*R*)-5, 4a, 5a- trihydroindeno- (1, 2-a) indane-2, 4, 9-triol-6-O-β-acetate (**1**) and has been designated as barbeyol.



Barbeyol (**1**): $C_{18}H_{16}O_5$ (M^+ 312)

Scheme 1.

Experimental Section

General

The IR spectra were recorded as KBr pellets on PYE UNICAM spectrophotometer. The mass spectra were recorded on a Finnegan MAT 300 mass spectrometer, and relative intensities have been given in parentheses. The ^{1}H (500 MHz) and ^{13}C & DEPT 90 and 135 NMR (125 MHz) and 2D NMR (COSY, HMBC & HMQC) were recorded on Bruker DRX 500 spectrometer in $CDCl_3$ and DMSO-d_6 using TMS as internal standard reference, chemical shift in δ (ppm) and coupling constants (J values) are in Hz. The elemental analysis was performed on a Perkin Elmer CHNSO analyzer, model no. 2400. Column chromatography was performed using silica gel (0.04–0.063 mm, 230–400 mesh) as an adsorbent. TLC were performed on silica gel 60 F_{254} Merck plates and sprayed with vanillin-H_2SO_4 reagents for visualization of the spots.

Plant material

The aerial parts of *Barbeya oleoides* Schweinf were collected in March 2000 from *Tanumah* and *Aseer* regions of Saudi Arabia and identified by a taxonomist Dr. Sultanul-Abedin, Medicinal, Aromatic and Poisonous Plants Research Center (MAPPRC), Department of Pharmacognosy, College of Pharmacy, King Saud University, Riyadh, Saudi Arabia. A voucher specimen no. 14122 has been deposited in the herbarium of the center for future reference.

Extraction and isolation

The dried aerial parts (3.0 kg) were crushed to coarse powder and extracted exhaustively with 95% alcohol in a percolator. The alcoholic extract was concentrated and dried under reduced pressure to get a viscous mass (500 g). It was then extracted with petroleum ether (150 g, oily and fatty material) and subsequently with methanol. The methanolic fraction (275.0 g) was chromatographed on a column of silica gel (1.8 kg, coated with 250 gm celite) and successively eluted with petroleum ether, dichloroethane (DCE) and methanol with increasing order of polarity (solvent for TLC: EtOAc-DCE, 1:1). The fraction (1.1 g) obtained at the eluent MeOH-DCE (1:1) was further purified by preparative TLC using RP (C-18) silica gel and 5% water in acetonitrile as developing solvent, which afforded compound **1** (Barbeyol, 300 mg).

*Barbeyol (***1***):* Obtained as yellow-red solid (300 mg) from benzene-methanol (1:1), R_f 1.5 (MeOH: DCE = 1:9); IR (KBr) ν_{max} 3390 (OH), 2950 (CH_3), 2840 (CH_2), 1704 (C=O) 1610 (C=C), 1523, 1451, 1468, 1375, 1282 (C-O, ester linkage), 1140 (C-O, phenolic), 1046 (C-O, alcoholic), 816, 765 cm^{-1}; 1D and 2D NMR data, see Table I; EIMS: *m/z* (rel. int.) 312 (6), 206 (10), 148 (5), 143 (6), 137 (12), 84 (4), 69 (7), 59 (15), 43 (100); HRMS: *m/z* 312.3244) (calcd. for $C_{18}H_{16}O_5$ 312.3241); Elemental analysis: Found: C 71.56%, H 4.74%, O 23.7%; required for: $C_{18}H_{16}O_5$; C 69.223%, H 5.16%, O 25.614%.

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