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1β,15α-DIHYDROXYFRIEDELAN-3-ONE, A TRITERPENE FROM *SALACIA BEDDOMEI*

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Key Word Index—*Salacia beddomei*; Celastraceae; triterpenes; 1β,15α-dihydroxyfriedelan-3-one.

Abstract—A new triterpene, 1β,15α-dihydroxy-friedelan-3-one, has been isolated from the stem bark of *Salacia beddomei*. Its structure has been elucidated on the basis of NMR and MS techniques. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Our previous reports on the constituents of the stem bark of *Salacia beddomei* (Gamble) deal with the isolation and characterization of several new lupane triterpenoids together with three known friedelanes, friedelan-3-one, 15α-hydroxyfriedelan-3-one (**2**) and 15α-hydroxyfriedelane-1,3-dione (**3**) [1, 2]. Purification of the fractions obtained during the above chromatographic fractionation yielded a new friedelane compound which has now been characterized as 1β,15α-dihydroxyfriedelan-3-one (**1**) on the basis of spectral evidences.

RESULTS AND DISCUSSION

Compound **1** gave a positive Libermann–Burchard reaction for triterpenes and on TLC gave an orange red spot when sprayed with 2,4-dinitrophenylhydrazine followed by heating, indicating a reactive oxo group in the molecule. Its ^{1}H and ^{13}C NMR spectra showed characteristic signals of a friedelane compound similar to **2** and **3**, thereby suggesting a friedelane skeleton for **1**.

The EI-mass spectrum of **1** shows the molecular ion at *m/z* 458 corresponding to the formula $C_{30}H_{50}O_3$, in agreement with other spectroscopic data. The ^{1}H NMR spectrum shows seven tertiary methyl singlets and a secondary methyl doublet. The presence of two secondary hydroxyl groups in **1** is evident in the ^{1}H NMR spectrum from the presence of two carbinol methine protons at δ 3.70 (*d*, *J* = 7.9 Hz) and 4.85 (*br s*) which is supported by the signals of two hydroxylated carbons at δ 71.3 and 74.7 in the ^{13}C NMR spectrum. The additional features of the ^{1}H NMR spectrum are the presence of a pair of one proton double doublets at δ 2.69 (*J* = 4.6, 13.9 Hz) and 2.40 (*J* = 2.4, 13.9 Hz), a one proton double doublet at δ 2.16 (*J* = 7.9, 15.8 Hz) and a one proton quartet at δ 2.32 (*J* = 7.2 Hz). The location of the functional groups in **1** were deduced from an analysis of the chemical shift data, decoupling studies and comparison with **2** and **3**.

The carbinol methine proton shift at δ 3.70 and the hydroxylated carbon chemical shift at δ 74.8 have been directly assigned for a 15α-hydroxyl substitution in **1** by analogy to the identical shifts observed for **2** and **3** [1, 3]. Moreover, the ^{13}C NMR shifts observed for the rings C, D and E are in good agreement with the corresponding shifts in **2** and **3** thus confirming a 15α-hydroxyl substitution.

A C-3 keto substitution in **1** is evident from the one-proton quartet at δ 2.32 due to H-4α and irradiation of this signal collapses the C-23 methyl doublet at δ 0.95 into a singlet as expected. The double doublets

Table 1. ^{1}H NMR data of compounds **1** and **2** ($CDCl_3$, TMS, 270 MHz)

H	**1**	**2**
1	4.85 (*brs*)	1.94 (*m*), 1.68 (*m*)
2	2.69 (*dd*, *J* = 4.6, 13.9 Hz)	2.40 (*m*)
	2.40 (*dd*, *J* = 2.4, 13.9 Hz)	2.20–2.28 (*m*)
4	2.32 (*q*, *J* = 7.2 Hz)	2.20–2.28 (*m*)
15	3.70 (*d*, *J* = 7.9 Hz)	3.73 (*d*, *J* = 7.9 Hz)
16	2.16 (*dd*, *J* = 7.9, 15.8 Hz)	2.15 (*dd*, *J* = 7.7, 16.1 Hz)
	1.25 (*m*)	1.25 (*m*)
23	0.95 (*d*, *J* = 7.2 Hz)	0.87 (*d*, *J* = 6.6 Hz)
24	1.10 (*s*)	0.73 (*s*)
25	1.33 (*s*)	0.89 (*s*)
26	1.08 (*s*)	1.07 (*s*)
27	0.99 (*s*)	1.00 (*s*)
28	1.30 (*s*)	1.29 (*s*)
29	1.03 (*s*)	1.02 (*s*)
30	0.96 (*s*)	0.95 (*s*)

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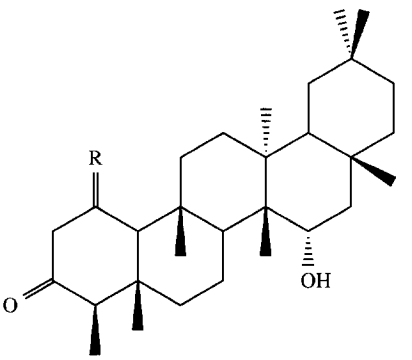
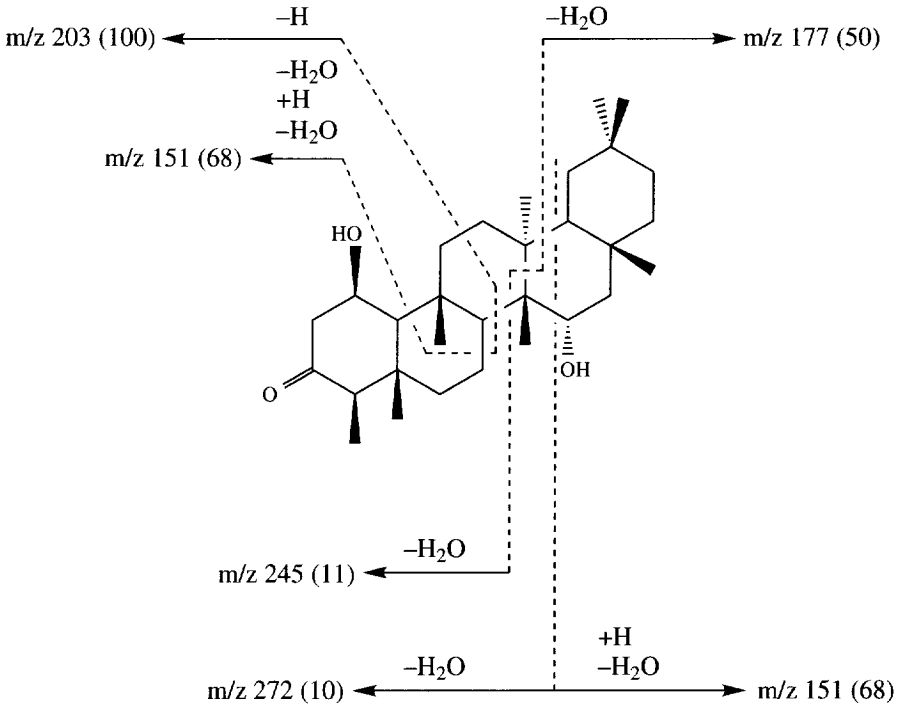


1 R = β – OH, H
2 R = H_2
3 R = O



Scheme 1. EI mass spectral fragmentation of compound **1** (relative intensities are given in parentheses).

at δ 2.69 and 2.40 can be assigned to the diastereotopic C-2 methylene protons and their mutual connectivity has been established by decoupling studies. The multiplicity of each C-2 proton as double doublets can be rationalized in terms of a further splitting due to a third proton, i.e. at C-1.

Confirmation of this assignment as well as the location of the remaining hydroxyl group at C-1 comes from irradiation of the broad carbinol methine signal at δ 4.80 which affects the splitting pattern of both double doublets at δ 2.69 and 2.40 and simplifies them into AB doublets.

The orientation of the C-1 hydroxyl group as β and axial has been assigned from the following observation. In comparison with the tertiary methyl protons shifts of **2**, the shifts of the C-24 and C-25 tertiary methyl groups in **1** have been found to be deshielded considerably and appear at δ 1.10 and 1.33 i.e., 0.45–0.48 ppm higher than the corresponding shifts in **2** (Table 1). This deshielding effect can be explained in terms of a 1–3 syn-diaxial interaction of the 24 and 25 methyl groups with the axially oriented 1β hydroxyl group. Further evidence comes from the *J* values of the coupled doublets of C-2 protons. The *J* values of 4.6

Table 2. ^{13}C NMR data for compounds **1** and **2** (69.5 MHz, $CDCl_3$)

C	1	2
1	71.3	22.3
2	52.7	41.5
3	*	213.0
4	58.9	58.2
5	44.0†	42.0
6	43.8†	41.3
7	20.4	20.0
8	54.1	53.5
9	38.9	37.8
10	61.2	59.4
11	35.6	35.7
12	31.0	31.2
13	40.6	40.6
14	44.1	44.1
15	74.8	74.6
16	48.4	48.4
17	30.2	30.2
18	41.6	41.6
19	35.6	35.6
20	28.1	28.1
21	31.9	31.9
22	38.9	38.8
23	7.0	6.8
24	17.2	14.5
25	19.2	18.0
26	14.0	14.0
27	18.8	18.7
28	32.6	32.6
29	30.9	30.9
30	35.6	35.6

* Signal obscured due to poor signal to noise ratio.

† May be reversed within column.

and 2.4 Hz can be explained in terms of axial–equatorial and equatorial–equatorial interaction of C-2 protons with an equatorially oriented 1α proton. Moreover, the ^{13}C NMR data (Table 2) as well as the mass spectral fragmentation pattern (Scheme 1) are in agreement with the assigned structure thereby characterizing **1** as 1β,15β-dihydroxyfriedelan-3-one.

EXPERIMENTAL

Collection, identification, and extraction of *Salacia beddomei* stem bark and the purification procedures used have been described previously [1, 2]. ^1H NMR: 270 MHz, $CDCl_3$ using TMS as int. standard; ^{13}C NMR: 69.5 MHz, $CDCl_3$ signal as reference, and the chemical shifts were assigned by comparison with compound **2**, [1]. EIMS: 70 eV.

Compound **1** was isolated from the $CHCL_3$–EtOAc fractions of the EtOAc extract and eluted after betulin [2]. Evaporation of the fractions yielded a crude solid material (7 mg) contaminated with lipid impurities. Purification of the material by prep. TLC on silica gel using EtOAc–hexane yielded **1** as an amorphous material (*ca* 1 mg) which could not be crystallized.

1β,15α-Dihydroxyfriedelan-3-one (**1**). ^1H NMR (270 MHz, $CDCl_3$): Table 1; ^{13}C NMR: Table 2; EI-MS *m/z* (rel. int.): 458 $[M]^+$ (2), 440 $[M - H_2O]^+$ (12), 425 $[M - H_2O - Me]^+$ (10), 422 $[M - 2H_2O]^+$ (30), 407 $[M - 2H_2O - Me]^+$ (30), 272 (10), 245 (11), 231 (18), 218 (24), 203 (100), 189 (35), 177 (50), 151 (68), 107 (41).

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