

Oleanane Triterpenoids from *Gordonia ceylanica*

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Abstract – Chemical investigation of hot hexane extract of the stem bark of *Gordonia ceylanica* afforded a new triterpenoid, 3 β -acetoxy-28-hydroxyolean-12-ene (1) and three other oleanane triterpenoids, 3 β -hydroxyolean-12-ene (2), 3 β -acetoxyolean-12-ene (3), and 3 β -acetoxyolean-12-en-11-one (4) which are new to the species. Structure of compound 1 was suggested by ^1H NMR, ^{13}C NMR and MS spectral data and confirmed by converting to previously reported compound, erythrodiol diacetate (5). Structures of 2, 3 and 4 were established by comparison of the spectral data with the previously reported compounds. Further the acid hydrolysate of 4 was identical with 3 β -hydroxyolean-12-en-11-one (6).

Key words – *Gordonia ceylanica*, Theaceae, triterpenoids, oleanans.

Gordonia ceylanica belongs to the family Theaceae which consist approximately 520 species under 25 genera in the tropical and warm temperate areas of the world. The twelve Theaceae species distributed in Sri Lanka are categorized under five different genera. Among them all species belong to genus *Gordonia*, *G. ceylanica*, *G. dassanayakei*, *G. speciosa*, and *G. elliptica* are endemic to the country (Dassanayake, 1996). "Mihiriya" is the local name for all *Gordonia* species and the color of the flower is used as adjective to differentiate the certain species. However though all the *Gordonia* species are being used in traditional medicine in Sri Lanka, no previous chemical investigation is reported on any of these endemic species. Therefore the chemical and biological investigation of Sri Lankan *Gordonia* species are of our great interest.

Experimental

Plant material

The stem bark of *G. ceylanica* was collected from Nuwara Eliya district in the Central Province of Sri Lanka and the voucher specimen was authenticated by comparison with the herbarium specimen, 8291, *Jayasuriya* (17.10.92) at the National Herbarium, Royal Botanic Gardens, Peradeniya Sri Lanka.

Extraction

Air dried and ground stem bark of *G. ceylanica* (1.0 kg) was successively extracted with hot hexane, dichloromethane and methanol. The concentrated hot hexane extract (4.82 g) was fractionated by medium pressure column packed with silica gel using gradient elution with hexane, dichloromethane and methanol. These fractions were further purified by small scale medium pressure, flash and thin layer chromatography to give following compounds.

3 β -Acetoxy-28-hydroxyolean-12-ene (1)

– Colorless needles, mp 144-146°C; ^1H NMR (300 MHz, CDCl_3) δ : 5.19 (1H, dd, $J=3.4$ & 3.2 Hz, H-12), 4.50 (1H, dd, $J=6.0$ & 8.0 Hz, H-3), 3.55 (1H, d, $J=10.8$ Hz, H-28), 3.21 (1H, d, $J=10.8$ Hz, H-28) 2.05 (3H, s, OCOCH_3),

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1.16, 0.95, 0.94 (each 3H, s, 3xCH₃), 0.92-0.82 (12H, br.s, 4xCH₃); ¹³C NMR (75 MHz, CDCl₃) table-1; MS (70 eV), m/z (rel. int.%): 484 (M⁺, 0.5), 234 (8), 203 (100), 189 (9), 105 (15), 81 (8).

3β-Hydroxyolean-12-ene (2) – Colorless needles, mp 194-195°C {Lit. Faujan *et al.*, 1995) mp 195-196°C}; ¹H NMR (300 MHz, CDCl₃) δ: 5.18 (1H, dd, *J*=3.6 & 3.6 Hz, H-12), 3.21 (1H, dd, *J*=10.2 & 5.7 Hz, H-3), 1.13 (3H, s, H-27), 0.99, 0.96, 0.93 (each 3H, s, 3xCH₃), 0.87 (6H, br.s., 2xCH₃), 0.83, 0.79 (each 3H, s, 2xCH₃); ¹³C NMR (75 MHz, CDCl₃) table-1; MS (70 eV), m/z (rel. int.%): 426 (M⁺, 10), 218 (100), 203 (35), 135 (25), 95 (45).

3β-Acetoxyolean-12-ene (3) – Colorless needles, mp 236-237°C {Lit. Shiojima *et al.*, 1996 (mp 238-240°)}; ¹H NMR (300 MHz, CDCl₃) δ: 5.18 (1H, dd, *J*=3.2 & 3.6 Hz, H-12), 4.50 (1H, dd, *J*=7.2 & 8.4 Hz, H-3), 2.05 (3H, s, OCOCH₃), 1.13 (3H, s, H-27), 0.96 (6H, s, H-25, H-26), 0.87 (12H, br.s., H-23, H-24, H-29 & H-30), 0.83 (3H, s, H-28); ¹³C NMR (75 MHz, CDCl₃) table-1; MS (70 eV), m/z (rel. int.%): 468 (M⁺, 3), 218 (100), 203 (42), 189 (17), 135 (19), 95 (45), 81 (33), 69 (52), 55 (30).

3β-Acetoxyolean-12-en-11-one (4) – Colorless needles, mp 272-273°C {Lit. Bandaranayake, 1980 (mp 269-272°)}; ¹H NMR (300 MHz, CDCl₃) δ: 5.58 (1H, s, H-12), 4.51 (1H, dd, *J*=11.5 & 5.1 Hz, H-3), 2.79 (1H, ddd, *J*=13.5, 3.6 & 3.6 Hz, H-18), 2.35 (1H, s, H-9), 2.04 (3H, s, OCOCH₃), 1.56, 1.35, 1.15, 1.13, 0.91, 0.88, 0.87, 0.85 (each 3H, s, 8xCH₃); ¹³C NMR (75 MHz, CDCl₃) table-1; MS (70 eV) m/z (rel. int.%): 482 (M⁺, 5), 273 (38), 232 (59), 217 (12), 175 (33), 135 (100), 121 (18), 95 (30), 81 (20), 55 (25), 43 (55).

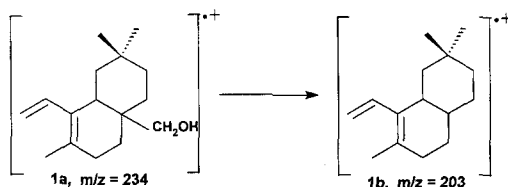
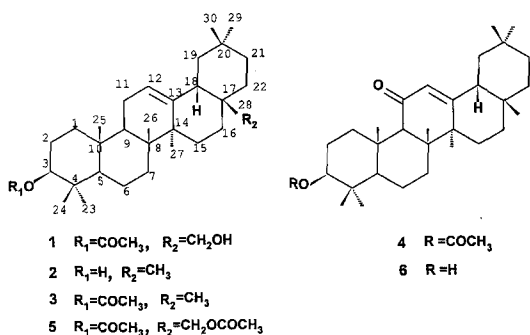
Erythrodiol diacetate (5) – Colorless needles, mp 186-187°C {Lit. Shiojima *et al.*, 1995 (mp 189-190°)}; ¹H NMR (200 MHz, CDCl₃) δ: 5.20 (1H, dd, *J*=3.5 & 3.5 Hz, H-12), 4.50 (1H, dd, *J*=7.0 & 9.5 Hz, H-3), 4.06 (1H, d, *J*=11.2 Hz, H-28), 3.70 (1H, d, *J*=11.4 Hz, H-28), 2.04 (6H, s, 2x OCOCH₃), 1.16 (3H, s,

Table 1. ¹³C NMR spectral data of compounds 1-6

Carbon No.	1	2	3	4	5	6
1	38.3	38.5	38.3	38.8	38.3	39.1
2	23.6	27.2	23.6	23.4	23.5	27.3
3	80.8	79.0	80.9	80.6	80.9	78.7
4	37.7	38.7	37.8	38.1	37.8	38.5
5	55.2	55.1	55.3	55.1	55.2	54.9
6	18.3	18.3	18.3	18.7	18.2	18.7
7	32.5	32.6	32.6	32.7	32.5	32.7
8	39.8	39.7	39.8	43.4	39.8	43.4
9	47.6	47.6	47.6	61.5	47.5	61.7
10	36.9	36.9	36.9	37.0	36.8	37.0
11	23.6	23.5	23.7	200.0	23.5	200.3
12	122.3	121.7	121.7	128.1	122.8	128.1
13	144.5	145.2	145.2	170.5	143.6	170.6
14	41.7	41.7	41.7	45.4	41.6	45.4
15	25.6	26.1	28.4	26.4	25.5	26.4
16	22.0	26.9	26.2	26.5	22.2	26.4
17	36.9	32.5	32.5	32.4	35.7	32.3
18	42.3	47.2	47.3	47.6	42.5	47.6
19	46.8	46.8	46.8	45.2	46.2	45.1
20	31.0	31.1	31.0	31.0	30.9	31.0
21	34.1	34.7	34.8	34.4	34.0	34.4
22	31.0	37.1	37.2	36.5	31.4	36.5
23	29.7	28.1	28.1	28.0	29.7	28.1
24	15.5	15.5	16.7	16.7	15.5	16.3
25	15.5	15.6	15.6	16.4	15.5	15.5
26	16.7	16.8	16.8	17.4	16.7	17.5
27	25.9	26.0	26.0	23.5	25.9	23.4
28	69.7	28.4	27.0	28.7	70.7	28.7
29	33.3	33.3	33.3	33.0	33.1	33.0
30	23.6	23.6	23.6	23.6	23.5	23.9
OCO	170.9	-	170.9	170.9	171.3	-
					171.0	
COCH ₃	21.3	-	21.3	21.3	21.3	-
					20.9	

CH₃), 0.96 (6H, br.s., 2xCH₃), 0.90-0.83 (12H, br.s., 4xCH₃); ¹³C NMR (50 MHz, CDCl₃) table-1; m/z (rel. int.%): 526 (M⁺, 6), 276 (11), 203 (100), 189 (14), 105 (21), 81 (7).

3β-hydroxyolean-12-en-11-one (6) – Colorless needles, mp 227-229°C {Lit. Bandaranayake, 1980 (mp 229-232°)}; ¹H NMR (200 MHz, CDCl₃) δ: 5.58 (1H, s, H-12), 3.28 (1H, m, H-3), 2.79 (1H, ddd, *J*=13.4, 3.4 & 3.4 Hz, H-18), 2.35 (1H, s, H-9), 1.14 (6H, s 2xCH₃), 1.36, 0.99, 0.91, 0.88, 0.85 and 0.79 (each 3H, s, 6xCH₃); ¹³C NMR (50 MHz, CDCl₃) table-1; MS (70 eV) m/z (rel. int.%): 440 (M⁺, 4), 273 (52), 232 (76), 175 (23), 135 (100), 121 (14).



Results and Discussion

The molecular formula $\text{C}_{32}\text{H}_{52}\text{O}_3$, suggested by the molecular peak at $m/z = 484$ in the mass spectrum of compound **1** was in concurrence with the thirty two corresponding signals appeared in the ^{13}C NMR spectrum. The presence of single olefinic proton (H-12) and the proton under the vicinity of the acetate group at C-3 were indicated by double doublets at δ 5.19 and 4.50 respectively while two protons attached to C-28 were represented by the two doublets at δ 3.55 and 3.21 in the ^1H NMR spectrum of **1**. Methyl protons of the acetate group of the molecule were appeared as 3H singlet at δ 2.05 while the other seven methyl groups were appeared in the region of δ 1.16 to 0.86 in the ^1H NMR spectrum of compound **1**. ^{13}C NMR spectrum of **1** also showed the presence of two olefinic carbons, C-12 and C-13 at δ 122.3 and 144.5 respectively. Further the C-3 carbon flanking the acetate group and C-28 containing hydroxyl group were appeared at δ 80.8 and 69.7 respectively in the ^{13}C NMR spectrum of **1**. The peak at m/z 234 in the MS spectrum was assigned for the fragment ion **1a** which gives as a result of retro Diels-Alder

fragmentation of compound **1**. The base peak at m/z 203 in the mass spectrum was analogous to the resulted ion **1b** by cleavage of CH_2OH moiety from **1a**. These mass spectroscopic evidence are also in consistent with other spectroscopic evidence suggested that the CH_2OH group in the molecule is flanking to the C-17 position. Further the acetylation of **1** to give erythrodiol diacetate (**5**) (Xue *et al.*, 1988 & Shiojima *et al.*, 1995) were strongly supported to confirm the structure proposed for compound **1**. The structures assigned for compound **2** and **3** were identical with the previously reported compounds, β -amyrin (Faujan *et al.*, 1995) and β -amyrin acetate (Shiojima *et al.*, 1996 & Agrawal *et al.*, 1992) respectively and confirmed by co-TLC with authentic samples. The presence of the carbonyl group at C-11 in the proposed structure for compound **4** was indicated by the signal at δ 200.0 in the ^{13}C NMR and further supported by the two sharp singlets at δ 2.35 and 5.58 in the ^1H NMR which appeared due to H-9 and H-12 respectively. Further the spectral data of compound **4** were identical with the reported data of the previously isolated compound 3- β -acetoxyolean-12-en-11-one (Bandaranayake, 1980) and also the spectral data of the acid hydrolysed product of compound **4** were identical with the previously reported values of 3- β -hydroxyolean-12-en-11-one (**6**) (Bandaranayake, 1980).

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