THREE NEW TETRAHYDOAZULENE DERIVATIVES AND ONE NEW BUTENOLIDE DERIVATIVE FROM *HORTONIA*, A GENUS ENDEMIC TO SRI LANKA

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Introduction

Hortonia is a genus endemic to Sri Lanka and is considered to have originated in Gondwanaland about 100-120 million years ago. Wight described three species of *Hortonia* (*H. floribunda*, *H. ovalifolia*, and *H. acuminata*) from the wet zone of Sri Lanka. The latest revision of the family Monimiaceae by Dassanayake (1996) lists three distinct species (*H. floribunda* Wight ex Arn, *H. angustifolia* (Thw.) Trimen and *H. ovalifolia* Wight) in Sri Lanka. The present study was initiated with a view to studying the chemistry of the genus *Hortonia* in Sri Lanka.

Materials and Methods

Specimens of *H. angustifolia*, *H. floribunda* and *H. ovalifolia* were collected from Kanneliya (Southern Province), Hakgala (Central Province), and the foothills of Adam's Peak (Central Province), respectively. Voucher specimens (*H. angustifolia* PDA 526; *H. floribunda* PDA 24083, *H. ovalifolia* PDA 522) were deposited at the National Herbarium, Peradeniya, Sri Lanka.

The ^{1}H, ^{13}C NMR, HMQC and HMBC spectra were recorded in Acetone-d_6 (**1, 2, 4**) and CD_2Cl_2 (**3**) at 400 (compounds **1**, **3** and **4**) and 600 (compound **2**) MHz on a Bruker spectrometer and were referenced to the solvent. HRESIMS were recorded on a Micromass LCT spectrometer. Arg-Lys (compound **1** and **2**), perflurokerosene (compound **3**) and Arg-Phe (compound **4**) were used as the internal reference for HRMS measurements.

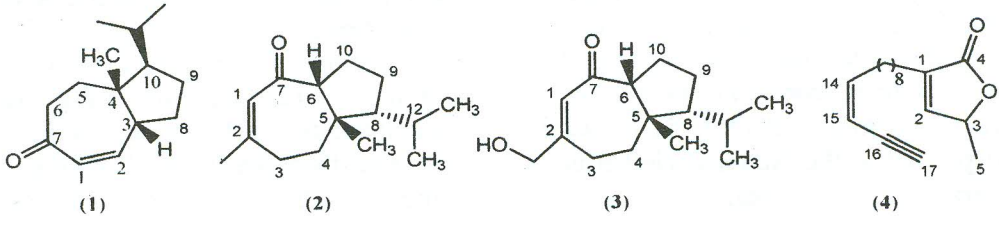
Air dried, powdered leaves of H. angustifolia (650 g) were extracted with CH_2Cl_2 (3 x 700 mL) at 27 ^{0}C for 24 h. The combined CH_2Cl_2 extracts were concentrated in vacuo to obtain black oil (30 g). This was subjected to MPLC on Si gel (eluent: step gradient from hexane to EtOAc) followed by Si gel flash chromatography (eluent: step gradient from hexane to EtOAc/hexane, 3:7) to provide pure compounds 1 (53 mg), 2 (8 mg), 3 (28 mg) and 4 (16 mg). Compounds 1-4 were similarly isolated from leaves of *H. floribunda* and *H. ovalifolia* in comparable yields using identical chromatographic conditions.

Results

Table 1.^{1}H and ^{13}CNMR Data for1.2.3

position	1a		2a		3b	
	d_C	d_H (*J* in Hz)	d_C	d_H (*J* in Hz)	d_C	d_H (*J* in Hz)
1	131.6	5.79, dt (11.9, 1.9)	129.6	5.75, s	126.1	6.03, s
2	152.4	6.38, dd (11.9, 4.9)	158.7		159.9	
3	51.8	2.64, m	32.9	2.62, dd (18.3, 10.8) 2.29, dd (18.7, 7.2)	27.7	2.45, dd (17.7, 11.3) 2.20, dd (18.2, 7.2)
4	48.8		41.9	2.00, m 1.43, dd (15.0, 11.0)	41.0	2.03, m 1.43, m
5	36.0	1.87, m 1.71, m	48.5		48.4	
6	40.4	2.49, dd (11.0, 1.5) 2.45, dt (7.2, 1.7)	65.1	2.75, dd (7.6, 2.4)	65.0	2.76, dd (7.6, 2.4)
7	204.2		203.4		204.5	
8	30.8	2.04, m	55.9	1.12, m	55.1	1.16, m
9	29.9	1.49, m 1.46, m	30.1	1.93, m 1.57, m	30.0	1.46, m
10	57.3	1.33, m	23.1	2.00, m 1.53, m	30.0	1.60, m
11	21.6	1.03, s	21.2	1.05, s	20.9	1.05, s
12	30.9	1.60, m	30.1	1.56, m	29.5	1.55, m
13	23.4	0.96, d (6.7)	23.5	0.91, d (6.6)	23.1	0.89, s
14	23.3	0.90, d (6.6)	23.4	0.87, d (6.7)	23.1	0.87, s
15			26.4	1.91, s	66.4	4.15, d (10.5)

[a]Spectra collected in Acetone-d_6 at 400MHz
[b]Spectra collected in CD_2Cl_2 at 600MHz



(1) (2) (3) (4)

Figure 1. Structures of the compounds

Table 2. ^{1}H and ^{13}C NMR Data for 4

position	4[a]	
	δ_C	δ_H (J in Hz)
1	134.1	
2	150.9	7.28, s
3	78.1	5.03, dq (6.6, 1.7)
4	174.0	
5	19.5	1.35, d (6.9)
6	25.8	2.22, t (7.7)
7	28.2	1.55, m
8-11	29.5-30.0	1.33, br. s
12	29.5	1.42, m
13	30.9	2.32, dq (7.4, 1.1)
14	146.4	6.04, dt (10.9, 7.6)
15	109.2	5.48, ddt (10.9, 2.4, 1.3)
16	81.1	
17	83.4	3.58, d (2.2)

[a]Spectra collected in Acetone-d_6 at 600MHz

Discussion

Previously we reported the isolation of several new butenolides from all three *Hortonia* species (Ratnayake *et al.* 2001; Ratnayake *et al.* 2008). The structures of compounds **1-4** were elucidated by extensive spectroscopic analysis (Figure 1). Isolation of the same compounds from the three species is of chemotaxonomic importance.

References

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