



ROTENOIDS FROM SEEDS OF *CLITORIA FAIRCHILDIANA*

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Abstract—A new rotenoid, 11-deoxyclitoriacetal, along with the known 6-deoxyclitoriacetal, was isolated from the seeds of *Clitoria fairchildiana*. Their structures were established by spectroscopic and chemical methods, and by comparison with data from the literature. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

As a result of our work on the constituents of the seeds of *Clitoria fairchildiana* [1], we report the isolation and characterization of a new rotenoid, 11-deoxyclitoriacetal (**1**) and 6-deoxyclitoriacetal (**2**) [2].

RESULTS AND DISCUSSION

Fractionation of a EtOAc extract from the dried and powdered seeds of *Clitoria fairchildiana* by adsorption chromatography on silica gel afforded compounds **1** and **2**.

Compound **1** was obtained as yellow needles and showed no colour reaction with FeCl_3 . The molecular formula was calculated as $\text{C}_{19}\text{H}_{18}\text{O}_8$ by a combination of EI mass ($[\text{M}]^+$ m/z 374) and ^{13}C NMR spectral data (Table 1). The UV spectrum of **1** showed single maxima at 278 nm (4.25) and 320 nm (sh, 3.80). The chromatographic behaviour of **1**, UV spectrum, IR 3420 (OH), 1674 ($>\text{C}=\text{O}$), 1610, 1578 and 1508 cm^{-1} (aromatic), ^1H NMR δ 5.80 (1H, *d*, $J=2.0$ Hz, H-6eq), 5.60 (1H, *bs*, H-6ax) and 4.60 (1H, *bs*, H-6a) [3, 4], ^{13}C NMR δ 69.2 (C, C-12a) and 75.7 (C, C-6a) [2–5] and 91.3 (CH, C-6) spectral data established that **1** is a rotenoid.

A broad singlet at δ 4.90 integrating for a single proton and its D_2O exchange indicated the presence of a 6-hydroxyl group. The ^1H NMR spectrum displayed, in addition to signals for three methoxyl groups, two doublets at δ 7.85 ($J=8.8$ Hz) and 6.40 ($J=2.3$ Hz) for H-11 and H-8, respectively. One double doublet at δ 6.65 ($J=2.3$ and 8.8 Hz) was attributed

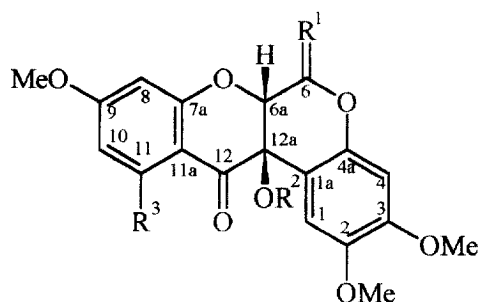
Table 1. ^{13}C NMR spectral data of compounds **1**–**2***

C	1	1a	2
1	110.1	110.0	109.4
1a	108.6	103.2	108.3
2	144.8	144.8	143.9
2-OMe	56.4	56.1	56.3
3	152.2	152.0	151.3
3-OMe	56.2	55.6	55.6
4	101.2	100.9	101.1
4a	148.8	148.1	148.3
6	91.3	88.2	63.6
6- COCH_3		168.9	
6- COCH_3		20.7	
6a	75.7	72.8	75.5
7a	162.3	159.9	161.5
8	92.3	94.5	94.2
9	167.6	168.8	168.9
9-OMe	56.1	55.9	55.6
10	111.9	110.0	95.4
11	129.7	128.6	164.2
11a	108.2	107.0	100.0
12	191.2	189.2	194.9
12a	69.2	65.7	66.9
12a- COCH_3		169.7	
12a- COCH_3		21.1	

* Assignments from DEPT, ^1H - ^{13}C COSY and ^1H - ^{13}C COLOC data.

to H-10. Two singlets at δ 6.70 and 6.45 integrating for single protons were assigned to H-1 and H-4, respectively. Based on the H-1 chemical shift value (δ 6.70), the B/C ring junction in **1** was determined to be *cis* [6–8]. The appearance of one doublet at δ 5.80 and a broad singlet at δ 5.60 attributed to

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- 1** $R^1 = H, \alpha OH; H, \beta OH; R^2 = R^3 = H$
1a $R^1 = H, \alpha OAc; H, \beta OAc; R^2 = Ac; R^3 = H$
2 $R^1 = H, H; R^2 = H; R^3 = OH$

H-6, and a broad singlet at δ 4.90, assigned to H-6a suggested the presence of two hydroxyl groups at C-6 and C-12a and that H-6 exists in **1** as H-6eq and H-6ax [7, 8].

These observations suggested that **1** exists as a mixture of two C-6 epimers in almost equal amounts. The assignment of chemical shifts of the methoxyl groups (Tables 1 and 2) was established by 2D-NMR correlations of **1** and by comparison of the data of **1** with those of 6-deoxyclitoriacetal [2].

Two prominent fragment ion peaks at m/z 151 and 224, due to cleavage between the B:C rings, revealed that ring D possessed only one methoxyl group (m/z 151), and rings A and B had two methoxyl and two hydroxyl groups (m/z 224). On acetylation, **1** gave the diacetate **1b**, which showed in its 1H NMR spectrum, two signals of two aliphatic acetyl groups at δ 2.32 and 2.20 assigned to the 12a and 6 positions, respectively.

Confirmation of this observation was supported by ^{13}C NMR and HR mass spectra. Consequently, on the basis of UV, IR, 1H and ^{13}C NMR spectroscopy, EIMS and chemical evidences, the structure of compound **1** was established as 11-deoxyclitoriacetal.

6-Deoxyclitoriacetal (**2**) previously reported as a constituent of *C. macrophylla*, was identified by direct comparison of UV, IR, 1H and ^{13}C NMR (Table 1 and Table 2) and EI mass spectral data with those related in the literature [2].

EXPERIMENTAL

General

Mps are uncorr. Optical rotations were measured at 20°. IR spectra were recorded in KBr discs. 1H NMR (200 MHz) and ^{13}C NMR (50 MHz), with TMS as int. standard and $CDCl_3$ as solvent. EIMS were recorded at 70 eV. Silica gel columns (230–400 mesh ASTM, Merck) were used for CC. TLC was performed on silica gel coated plates (Merck) using $CHCl_3$ -MeOH (19:1) for compounds **1** and **2** and $CHCl_3$ -MeOH (97.5:2.5) for **1a**; they were detected under UV 254 nm and 366 nm and by spraying with orcinol- H_2SO_4 .

Plant material

Seeds of *C. fairchildiana* Howard were collected at Ilha do Fundão, Rio de Janeiro, on July 1995, and identified by Luci Mendonça de Senna. A voucher specimen (no. R190871) is deposited at the Museu Nacional, Rio de Janeiro, Brazil.

Table 2. 1H NMR spectral data of compounds **1–2***†

H	1	1a	2
1	6.70 <i>s</i>	6.91 <i>s</i>	6.66 <i>s</i>
2-OMe	3.70 <i>s</i>	3.78 <i>s</i>	3.66 <i>s</i>
3-OMe	3.75 <i>s</i>	3.84 <i>s</i>	3.75 <i>s</i>
4	6.45 <i>s</i>	6.55 <i>s</i>	6.41 <i>s</i>
6	5.60 <i>bs</i> 5.80 <i>d</i> (2.0)	6.42 <i>bs</i> 6.59 <i>d</i> (2.0)	4.39 <i>dd</i> (2.0, 12.0) 4.51 <i>dd</i> (2.5, 12.0)
6-OH	4.90 <i>bs</i>		
6-OAc		2.20 <i>s</i>	
6a	4.60 <i>bs</i> 4.80 <i>d</i> (2.0)	5.40 <i>bs</i> 5.62 <i>d</i> (2.0)	4.49 <i>d</i> (2.0)
8	6.40 <i>d</i> (2.3)	6.65 <i>d</i> (2.2)	5.88 <i>d</i> (2.3)
9-OMe	3.80 <i>s</i>	3.81 <i>s</i>	3.75 <i>s</i>
10	6.65 <i>dd</i> (2.3, 8.8)	6.43 <i>dd</i> (2.3, 7.8)	6.04 <i>d</i> (2.3)
11	7.85 <i>d</i> (8.8)	7.50 <i>d</i> (7.8)	
11-OH			11.50 <i>s</i>
12a-OH	8.25 <i>s</i>		7.80 <i>s</i>
12a-OAc		2.32 <i>s</i>	

* J (Hz) in parentheses

† Assignments from 2D-COSY, 1H - ^{13}C COSY and 1H - ^{13}C COLOC experiments.

Isolation of constituents

Dried and powered seeds (470.8 g) were extracted with cold EtOAc. Evapn of the EtOAc gave a residue (25 g). A part of the residue (8 g) was submitted to CC (90 × 1 cm) of silica gel, eluted with CHCl₃-MeOH (97.5:2.5), which yielded two TLC homogeneous compounds, **1** (617 mg), R_f=0.35 and **2** (477 mg), R_f=0.75.

11-Deoxyclitoriacetal (1)

Pale yellow needles from CHCl₃, mp 75°. [α]_D + 8.0° (CHCl₃; *c* 0.001). UV_{max}^{EtOH} nm (log ϵ): 230(4.23), 278(4.25), 320(sh, 3.80). IR ν_{max}^{KBr} cm⁻¹: 3420 (OH), 3015, 2850, 1674 (>C=O), 1610, 1578, 1508, 1462, 1257, 1220, 1164, 1097, 1070, 1034. EIMS (probe) 70 eV *m/z* (rel. int.): 374 [M]⁺ (34), 356 [M-H₂O]⁺ (30), 327 [M-H₂O-CHO]⁺ (70), 224 [RDA fragment]⁺ (100), 207 [RDA fragment- OH]⁺ (29), 151 [RDA fragment 150+H]⁺ (92); HRMS found: [M]⁺ 374.3497, C₁₉H₁₈O₈ requires 374.3499. ¹H and ¹³C NMR in Tables 1 and 2. Compound **1** was acetylated with Ac₂O-4-dimethylaminopyridine for 72 hr to give **1a**, mp 50° from CHCl₃, R_f=0.25. HRMS found: [M]⁺ 458.4303, C₂₃H₂₂O₁₀ requires 458.4305. ¹H and ¹³C NMR in Tables 1 and 2.

6-Deoxyclitoriacetal (2)

Pale yellow needles, mp 132–133° from CHCl₃-EtOH (19:1) [2]. [α]_D + 232° (CHCl₃; *c* 0.1) [2]. EIMS

70 eV (probe) *m/z*: 374; HRMS found: [M]⁺ 374.1001; C₁₉H₁₈O₈ requires 374.1002. In addition to EIMS, UV, IR, EIMS and ¹H and ¹³C NMR (Tables 1 and 2), spectral data were in accordance with those in ref. [2].

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