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NARINGENIN COUMAROYLGLUCOSIDES FROM *MABEA CAUDATA**

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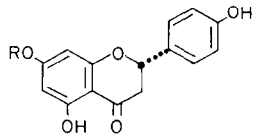
Key Word Index—*Mabea caudata*; Euphorbiaceae; naringenin; naringenin 7-*O*-(*p*-coumaroylglucosides).

Abstract—The fruits of *Mabea caudata* contain, besides 5,7,4′-trihydroxyflavanone (naringenin), naringenin 7-*O*-β-(3,6-di-*p*-coumaroylglucoside) and naringenin 7-*O*-β-(3-*p*-coumaroylglucoside).

INTRODUCTION

The genus *Mabea* Aubl. comprises 50 species distributed over tropical Central and South America [2]. One of these species, *M. caudata* Peth., is well represented in Amazonian forest regions. Fruits of the tree yielded (2*S*)-5,7,4′-flavanone (naringenin, **1a**) and two novel compounds (**1b**, **1c**).



1a R=H

1b R=β-3, 6-Di-*p*-Coumaroylglucosyl

1c R=β-3-*p*-Coumaroylglucosyl

RESULTS AND DISCUSSION

Acid hydrolysis of **1b** and **1c** gave, besides glucose and *p*-coumaric acid, naringenin. In both compounds the C-7 hydroxyl group of the naringenin moiety must be substituted, since, as with the aglycone, UV $AlCl_3$ shifts are observed, but, unlike the aglycone, the UV spectra are not changed upon addition of NaOAc. All 270-MHz ^1H NMR spectral features of **1b** are amenable to first-order analysis (Table 1) and led to assignments which were confirmed by the complete series of decoupling experiments. The signals due to H-3 (δ 5.28) and both H-6 (δ 4.37, 4.60) of the glucose moiety appear at relatively low field demonstrating esterification of the hydroxyls at these sites by *p*-coumaric acid. The analysis of the analogous spectrum of **1c** is less straightforward, only H-1 and H-2 giving fully resolved signals (respectively at δ 5.26 and 3.70). Here only one of the carbinolic protons of the glucose moiety is represented by a signal at relatively low field (δ 5.23). This must belong to H-3 since double irradiation at this frequency affected the H-2 signal and vice versa.

With respect to stereochemical features, the protons on the anomeric carbons in both, **1b** and **1c**, occupy α-positions, in view of their axial–axial relationships with H-2 ($J = 8$ Hz, Table 1). The 2*S*-configurational assignment for naringenin (**1a**) results from the observation of a positive Cotton effect for the $\pi \rightarrow \pi^*$ transition [3].

EXPERIMENTAL

Isolation of the constituents. Fruits of *M. caudata* were collected by Hipólito F. Paulino Filho near Humaitá, Amazonas State, from a specimen identified by Dr. William A. Rodrigues, INPA, Manaus. The powder (250 g), obtained from dry fruits, was percolated in succession with C_6H_6 and EtOH. The EtOH extract (6.5 g) was suspended in Me_2CO and filtered. The Me_2CO extract (5 g) was chromatographed on a dry column (100 g Si gel deactivated with 10% H_2O, C_6H_6–EtOAc, 1:1). The extruded column was cut into 6 equal segments numbered 1–6 from column bottom to top. The segments were eluted with Me_2CO. Eluate 1 (120 mg) was washed with $CHCl_3$ and purified by prep. TLC (Si gel, C_6H_6–Me_2CO, 7:3) to give **1a** (16 mg). Eluates 2 and 3 (2.5 g), repeatedly chromatographed in the same way, yielded slightly less polar **1b** (375 mg) and slightly more polar **1c** (250 mg).

Naringenin (**1a**), mp 246–248° (MeOH) (lit. [4] mp 248°). ORD (MeOH, 250): $|\phi|^{pk}_{300} + 2000$, $|\phi|_{316}$ 0, $|\phi|^{tr}_{330} - 1100$, $|\phi|^{sh}_{345} - 340$, $|\phi|_{353}$ 0, $|\phi|^{pk}_{370} + 400$.

Naringenin 7-O-β-(3,6-*di*-p-*coumaroylglucose* (**1b**), mp 155–158° (CCl_4–Me_2CO 8:2). [Found: C, 64.91; H, 4.85. $C_{39}H_{34}O_{14}$ requires: C, 64.46; H, 4.72%.] UV λ^{MeOH}_{max} nm: 285, 310 (ε 50 000, 40 750); no NaOAc shift; $\lambda^{MeOH+AlCl_3}_{max}$ nm: 305 (ε 50 300). IR ν^{KBr}_{max} cm^{-1}: 3509, 1712, 1642, 1616, 1517, 1443, 1250 (*br*), 837. *Acetate* (**1b**, Ac_2O, C_5H_5N, 24 hr, room temp.), mp 116–118° (CCl_4–Me_2CO, 8:2). IR ν^{KBr}_{max} cm^{-1}: 1795, 1629, 1529, 1462, 1397, 1328, 1200 (*br*), 923, 853.

*Part 4 in the series "The Chemistry of Brazilian Euphorbiaceae". For part 3 see ref. [1]. Based on part of the M.Sc. thesis presented by D.A.D.B., on leave of absence from Faculdade de Farmácia e Odontologia de Riberirão Preto, to Universidade de São Paulo (1981).

Table 1. ^{1}H NMR data of **1a**, **1b**, **1c** and derivatives [270 MHz (**1b**, **1c**) and 60 MHz (**1a** and acetates)], in Me_2CO-d_6 (**1a–1c**) or $CDCl_3$ acetates, TMS an int. standard]*

Assignments	**1a**	Acetate of **1a**	**1b**	Acetate of **1b**	**1c**	Acetate of **1c**
Naringenin						
H-2	5.46 *dd* (12, 4)	5.60 *dd* (14, 4)	5.40 *dd* (12.5, 3)	5.2–5.4 *m*	5.50 *dd* (12.5, 3)	5.2–5.4
H-3	2.66 *dd* (14, 4)	2.6–3.3 *m*	2.77 *dd* (17, 3)	2.7–3.2 *m*	2.79 *dd* (17, 3)	2.7–3.2 *m*
H-3	3.20 *dd* (14, 12)		3.21 *dd* (17, 12.5)		3.25 *dd* (17, 12.5)	
HO-5	11.8 *s(br)*	—	11.5 *s*	—	11.5 *s*	—
H-6	5.93 *s*	6.63 *d* (3)	6.20 *d* (2)	6.35 *d* (3)	6.17 *d* (2.5)	6.36 *d* (3)
H-8		6.80 *d* (3)	6.25 *d* (2)	6.43 *d* (3)	6.21 *d* (2.5)	6.43 *d* (3)
H-2′, H-6′	7.35 *d* (8.5)	7.51 *d* (9)	7.51 *d* (8.5)	7–7.5 *m*	7.40 *d* (8.5)	7.5 *d* (8)
H-3′, H-5′	6.80 *d* (8.5)	7.20 *d* (9)	6.90 *d* (9)		6.90 *d* (9)	7.2 *d* (8)
AcO-5	—	2.36 *s*	—	2.35 *s*	—	2.36 *s*
AcO	—	2.30 *s*	—		—	2.33 *s*
AcO	—	2.16 *s*	—	—	—	—
Glucose						
H-1			5.32 *d* (7.5)	5.2–5.4 *m*	5.26 *dd* (7.5, 4.5)	5.2–5.4 *m*
H-2			3.78 *dd* (9, 7.5)		3.70 *dd* (9.5, 7.5)	
H-3			5.28 *t* (9)		5.23 *m*	
H-4			3.78 *dd* (9, 7.5)		3.92 ~ *d* (7.5)	
H-5			4.08 *ddd* (9.5, 6, 2)		3.75 *m*	
H-6			4.37 *dd* (12, 2)	4.3–4.6 *m*		4–4.3 *m*
H-6			4.60 *dd* (12, 6)			
AcO			—	2.03 *s*	—	2.03 *s*
AcO			—		—	
AcO			—	—	—	
p-Coumarate						
H-α			6.38 *d* (16)	6.3 *d* (16)	6.38 *d* (16)	6.33 *d* (16)
			6.40 *d* (16)		—	—
H-β			7.62 *d* (16)	7.7 *d* (16)	7.65 *d* (16)	7.70 *d* (16)
			7.67 *d* (16)		—	—

Table 1—(*continued*)

Assignments	1a	Acetate of 1a	1b	Acetate of 1b	1c	Acetate of 1c
H-2, H-6			7.37 *d* (8.5)		7.55 *d* (8.5)	7.6 *d* (8)
			7.56 *d* (8.5)		—	—
				7.75 *m*		
H-3, H-5			6.90 *d* (8.5)		6.90 *d* (8.5)	7.2 *d* (8)
			6.90 *d* (8.5)		—	—
			—		—	2.33 *s*
AcO				2.35 *s*		
			—		—	—

*Coupling constants (Hz) in brackets.

Naringenin 7 - O - β - (3 - p - *coumaroylglucose*) (**1c**), mp 162–164° (EtOH) [Found: C, 62.56; H, 5.01. $C_{30}H_{28}O_{12}$ requires: C, 62.07; H, 4.86%.] UV λ_{max}^{MeOH} nm: 285, 310 (ε 26 400, 18 200); no NaOAc shift; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 305 (ε 32 300). IR ν_{max}^{KBr} cm^{-1}: 3450, 1701, 1650, 1618, 1517, 1449, 1250 (*br*), 832. *Acetate* (**1c**, Ac_2O, C_5H_5N, 24 hr, room temp.), mp 138–141° (CCl_4). IR ν_{max}^{KBr} cm^{-1}: 1761, 1695, 1623, 1570, 1515, 1449, 1200 (*br*), 917, 845.

Hydrolysis of **1b** *and* **1c**. A suspension of the compound (80 mg) in H_2O–conc. HCl, 9:1 (7 ml) was heated under reflux for 4 hr [5], cooled and extracted with EtOAc. The presence of glucose was demonstrated in the aq. soln by direct TLC (Si gel, n-$C_5H_{11}OH$–AcOH–H_2O, 4:1:5) comparison with an authentic sample. The EtOAc extract (*ca* 45 mg) was separated by prep. TLC (Si gel, C_6H_6–Me_2CO, 7:3) into less polar **1a** and more polar *p*-coumaric acid. Both compounds were identified by direct comparison with authentic samples.

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