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ALKYL CHROMONE AND OTHER COMPOUNDS FROM *CLUSIA NEMOROSA*

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Key Word Index—*Clusia nemorosa*; Guttiferae; chromone; ferulate; terpenes; flavonoid.

Abstract—From *Clusia nemorosa* a new alkyl chromone, 5,7-dihydroxy-2-(*n*-heptaeicosanyl)chromone, and *n*-octacosanoyl ferulate were isolated, besides kaempferol, friedelin, friedelin-3β-ol, β-sitosterol glucoside and betulinic acid. Their structures were elucidated through analysis of spectroscopic data. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Clusia is a genus of approximately 200 species, distributed in the tropical and subtropical regions [1]. Some of them are used in the treatment of leprosy, for the cauterization of wounds and for the relief of headaches [2]. Species of this genus are known as sources of true and modified polyisoprenylated benzophenones [3–8], terpenes [1–2, 9–12], benzoquinone [9], flavonoids [13], dihydrophenanthrene derivative [14], and tocotrienolic acids [15]. *C. nemorosa* Mey., popularly known as 'pororoca' [16], is a tree widely spread in the northeast region of Brazil. In previous studies, this species had been found to contain only polyisoprenylated benzophenones and alkylarylketones [17–19]. In the present study an alkyl chromone (**1**) together with kaempferol, β-sitosterol glucoside, and betulinic acid from the leaves, and octacosanoyl ferulate (**2**), friedelin, friedelin-3β-ol, betulinic acid from the bark are reported. Lactonization of betulinic acid was carried out and the previously unreported NMR data of the product, 3β-acetoxy-12,13-dihydro-olean-28 → 19-β-lactone, are given.

RESULTS AND DISCUSSION

The UV spectra of **1** were compatible with a 5,7-dihydroxychromone derivative. In the IR spectrum absorptions for hydroxyls, a conjugated carbonyl, and aromatic and aliphatic groups were observed. Moreover, the ^{1}H NMR spectrum provided evidence for the presence of a chromone moiety substituted at C-2 [AB system with doublets centred at δ 6.12 and 6.03 (J = 2.1 Hz) and a singlet for an olefinic proton at δ 5.79] (Table 1). The presence of a long alkyl chain was evidenced by the triplets at δ 0.67 (J = 6.1 Hz) and 2.38 (J = 7.3 Hz), and by a very intense signal at δ 1.06 assigned to a terminal methyl and methylene groups, respectively. The chemical shifts of each carbon in the ^{13}C NMR spectra (Table 1) are in agreement with those of 5,7-dihydroxy-2-alkylchromone [20]. In the mass spectrum the peak of highest mass was found at m/z 556 (4%). Furthermore, the presence of the base peak at m/z 205 formed by cleavage of the side-chain between the β- and γ-carbon atoms and successive losses of C_1 units was observed.

The octacosanoyl ferulate **2** was identified on the basis of its spectral data and comparative analysis with literature values [21–23]. Only the previously unreported ^{13}C NMR data are given in Table 1.

The four known terpenes [24, 25] and kaempferol [26, 27] were identified from their spectral properties and comparison with those of the corresponding compounds recorded in previous reports.

EXPERIMENTAL

General. Mp uncorr.; UV: MeOH; IR: KBr; ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz): TMS as int. standard; MS: direct inlet, 70 eV.

Plant material. Leaves and bark of *C. nemorosa* Mey. were collected at the Reserva Biológica de Murici, Alagoas State, Brazil, and identified by Rosangela P. de Lira Lemos of the Instituto do Meio Ambiente (IMA/AL), where a voucher specimen (MAC-8734) was deposited.

Extraction and isolation. The air-dried powdered of the leaves (1750 g) and bark (1000 g) were extracted

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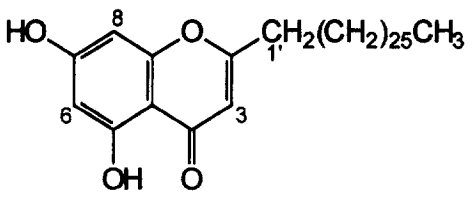

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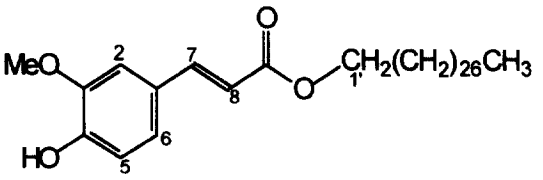

2

with 90% EtOH at ambient temp. After removal of the solvents *in vacuo*, the residues were suspended in MeOH–H_2O (3:2) and extracted with C_6H_{14}, $CHCl_3$ and EtOAc. The $CHCl_3$ residues (leaves; 31.1 g, bark; 14.5 g) were chromatographed on a silica gel column with C_6H_{14} containing increasing amounts of EtOAc. The residues from the CC frs were further purified by gel filtration on Sephadex LH-20 (MeOH) and repeated recrystallizations from MeOH to afford **1** (18.7 mg), betulinic acid (84.8 mg), kaempferol (43.2 mg) and β-sitosterol glucoside (99.2 mg) from the leaves, and friedelin (159.4 mg), a mixt. of **2** and friedelin-3β-ol (28.3 mg) and betulinic acid (2155 mg) from the bark.

5,7-*Dihydroxy*-2-(n-*heptaeicosanyl*)*chromone* (**1**). Amorphous powder, mp 301–304° (MeOH). UV λ_{max} (log ε): 207 (3.94), 221 (4.24), 255 (4.22), 297 (3.92); (MeOH + NaOAc): 228 (4.44), 249 (3.42), 272 (3.75), 345 (3.14), 370 (3.40); (MeOH + $AlCl_3$): 221 (4.25), 265 (3.27), 365 (3.27). IR ν_{max}^{KBr} cm^{-1}: 3347, 2928, 2852, 1654, 1628, 1582, 1471, 1385, 1168 and 1062. EIMS (probe) 70 eV, *m/z* (rel. int.): 556 $[M]^+$ (4), 555 (2), 527 (1), 499 (1), 485 (1), 471 (1), 401 (3), 387 (3), 373 (3), 359 (4), 345 (4), 331 (4), 317 (5), 303 (4), 261 (10), 219 (7), 206 (17), 205 (100), 193 (5), 192 (31), 164 (2), 163 (7), 152 (3); ^1H NMR (200 MHz, $CDCl_3$ + CD_3OD) and ^{13}C NMR (50.3 MHz, $CDCl_3$ + CD_3OD): Table 1.

Lactonization of betulinic acid. Betulinic acid (118 mg) was lactonized as described by Pakrashi *et al.* [28]. Recrystallization several times from $CHCl_3$–MeOH gave an amorphous powder (109 mg) of 3β-acetoxy-12,13-dihydro-olean-28 → 19-β-lactone, mp 314–317°. Lit. [28] mp > 330° ($CHCl_3$–MeOH). ^1H NMR (200 MHz, $CDCl_3$) δ: 4.49–4.41 (*m*, H-3), 3.90 (*br s*, H-19), 1.0, 0.93, 0.89, 0.82, 0.81 (*s*, 3H each), 0.85 (*s*, 6H) signals for seven methyl groups and 2.01 (*s*, MeCOO); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 179.7 (*s*,

Table 1. NMR data for compounds **1** and **2** [200 (^1H) and 50.3 (^{13}C) MHz; TMS as int. stand.]

H	**1** ($CDCl_3$/CD_3OD)	C	**1*** ($CDCl_3$/CD_3OD)	DEPT	**2**† ($CDCl_3$)	DEPT
3	5.79 *s*	1	—	—	127.0	C
6	6.12 *d* (2.1)‡	2	170.6	C	109.2	CH
8	6.03 *d* (2.1)	3	107.1	CH	146.7	C
1′	2.38 *t* (7.3)	4	182.4	C	147.9	C
2′–26′	1.06 *br s*	4a	106.0	C	—	—
27′	0.67 *t* (6.1)	5	161.3	C	114.7	CH
		6	98.8	CH	125.6	CH
		7	163.9	C	144.6	CH
		8	93.8	CH	115.7	CH
		8a	158.2	C	—	—
		9	—	—	167.4	C
		1′	33.8	CH_2	64.6	CH_2
		2′	31.5	CH_2	31.9	CH_2
		26′	22.2	CH_2		
		27′	13.5	CH_3	22.3	CH_2
		28′	—	—	14.1	CH_3
		MeO-3	—	—	55.9	CH_3

* Signals of the side-chain: δ 29.7 (CH_2, several), 29.4 (5 × CH_2), 29.3 (2 × CH_2), 28.8 (CH_2), 28.6 (CH_2) and 26.0 (CH_2).

† Signals of the side chain: δ 29.3 (CH_2, several), 29.0 (CH_2), 28.9 (CH_2), 28.8 (CH_2), 28.6 (CH_2) and 26.4 (CH_2).

‡ Coupling constant (*J*) in Hz.

C-28), 85.9 (*d*, C-19), 80.8 (*d*, C-3), 55.0 (*d*, C-5), 51.2 (*d*, C-9), 46.7 (*d*, C-18), 46.1 (*s*, C-17), 40.6 (*s*, C-8), 39.9 (*s*, C-4), 39.8 (*t*, C-1), 37.8 (*s*, C-10), 37.2 (*s*, C-14), 36.0 (*d*, C-13), 35.7 (*s*, C-20), 33.5 (*t*, C-7), 32.3 (*t*, C-16), 31.9 (*t*, C-15), 28.7 (*q*, C-29), 27.9 (*t*, C-21), 27.8 (*q*, C-23), 26.5 (*t*, C-22), 25.5 (*t*, C-12), 23.9 (*q*, C-30), 23.6 (*t*, C-2), 20.9 (*t*, C-11), 18.0 (*t*, C-6), 16.6 (*q*, C-25), 16.4 (*q*, C-26), 15.5 (*q*, C-24), 13.6 (*q*, C-27), 170.9 (*s*, CH_3COO), 21.2 (*q*, CH_3COO).

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