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SHORT COMMUNICATION

XANTHONES FROM *CARAIPA DENSIFLORA*[*]

R. Alves de Lima[†] and O. R. Gottlieb

Escola de Pós-Graduação, Universidade Federal Rural do Rio de Janeiro, c.p. 25, ZC-00,
Rio de Janeiro, Brasil

and

A. A. Lins Mesquita

Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil

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Key Word Index—*Caraipa densiflora*; Guttiferae; triterpenoids; vanillin; 1,6-dihydroxy-7,8-methylenedioxyxanthone; 1,5-dihydroxy-6,7-dimethoxyxanthone.

Abstract—The trunk wood of *Caraipa grandifolia* Mart. (Guttiferae) contains sitosterol, lupeol, lupenone. betulinic acid and vanillin. The trunk wood of *C. densiflora* Mart. contains sitosterol, lupeol, friedelin, betulinic acid, vanillin, 1,6-dihydroxy-7,8-methylenedioxyxanthone and 1,5-dihydroxy-6,7-dimethoxyxanthone.

THE GENUS *Caraipa* (Guttiferae) comprises some 30 species, mostly trees, which grow predominantly in the Amazon region, but may spread as far south as the State of Pernambuco.[3] *C. grandifolia* Mart., which occurs around the estuary of the Amazon, contains in its trunk wood sitosterol, lupeol, lupenone, betulinic acid and vanillin. *C. densiflora* Mart., from the surroundings of Cabo, Pernambuco State, contains sitosterol, lupeol, friedelin, betulinic acid and vanillin, and in addition two novel compounds, $C_{14}H_8O_6$ and $C_{15}H_{12}O_6$.

The small quantity (1·5 mg) and the insolubility of the compound $C_{14}H_8O_6$ precluded its NMR spectroscopical examination. The UV spectrum, however, was very informative, since it not only suggested a xanthone structure, but also indicated the presence of two hydroxyls at *ortho* ($AlCl_3$-shift) and *para* (NaOAc-shift) positions relative to the carbonyl.[4] The batho- and hyperchromic shift upon addition of NaOAc was compatible only with it being either a 1,6-dihydroxyxanthone, or a 1,3-dihydroxyxanthone, with an additional oxyfunction at C-2 or C-4.[5] The latter alternative, however, cannot be correct, since the mole-

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[†] Present address: Departamento de Química, Instituto de Ciências Exatas, Universidade de Brasília, Brasília, Brasil.

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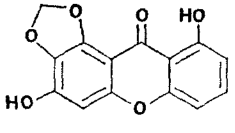
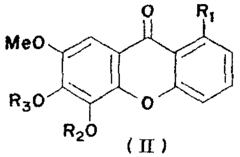
cular formula of the compound and the IR spectrum (ν_{max} 947 cm^{-1})[6] requires this oxy-function to be a methylenedioxy-group which cannot be included in a 1,3-dihydroxylated ring. Besides, the relatively high absorbance in the Gibbs test indicated the existence of an unsubstituted C-4, free of steric hindrance by a substituent at C-3.[4] On the basis of these data, the constitution I is proposed for the compound.

In view of this result it seemed attractive to consider also the 1,2,3,8-oxygenation pattern for the dihydroxy-dimethoxyxanthone $C_{15}H_{12}O_6$. The dimethyl ether, however, was not identical with 1,2,3,8-tetramethoxyxanthone (see Experimental), but with 1,5,6,7-tetramethoxyxanthone (IIa). This was established by analysis of the NMR spectrum which showed the singlet (τ 2·48) due to an isolated proton at the *peri*-position of a trioxygenated xanthone ring, and the three quartets (τ 2·38, 2·88 and 3·19), whose chemical shifts and coupling constants identify the group of 3 vicinal protons of a C-1 oxygenated xanthone ring.[7] While one of the hydroxy groups must occupy this C-1 position ($AlCl_3$ + HCl shift of UV maxima), the other hydroxyl may be situated either at C-5 or at C-6. The observed strong bathochromic shift of the UV K band is not consistent with the presence of a feebly acidic 7-hydroxyl.[4] A tentative selection between the remaining constitutional alternatives IIb and IId was made through spectral comparison with two model compounds, IIc and IIe (Table 1). The acidity, expressed in terms of NaOAc shifts,[5] likened the new compound to IIc, pointing to the 5-hydroxylated alternative (IIb). The stability of the methoxyl groups, expressed in terms of relative intensity of the M, M-15 and M-30 peaks in the mass spectrum, again pointed to the 6,7-dimethoxylated alternative (IIb). Finally, a sample of the compound

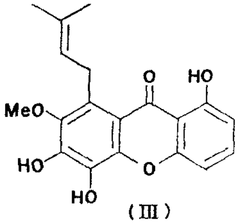


(I)



(II)

	R₁	R₂	R₃
(IIa)	OMe	Me	Me
(IIb)	OH	H	Me
(IIc)	H	H	Me
(IId)	OH	Me	H
(IIe)	H	Me	H



(III)

TABLE 1. SPECTRAL COMPARISON OF THE COMPOUND $C_{15}H_{12}O_6$ WITH MODEL XANTHONES

	UV shifts*		Peak intensities of MS		
	$\lambda_{K'}$-λ_K	$\epsilon_{K'}/\epsilon_K$	M	M-15	M-30
$C_{15}H_{12}O_6$ (IIb)	36	1·0	100	10	19
IIc[8]	25	0·7	100	25	2
IIe[9]	66	1·6	56	16	100

* Comparison of wavelength (nm) and extinction coefficients of the K band in the UV spectra (in EtOH) in the absence (K) and in the presence (K′) of NaOAc.[5]

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was submitted to Dr. F. Scheinmann, who kindly informed us that it is indeed identical with synthetic 1,5-dihydroxy-6,7-dimethoxyxanthone.[10]

1,5-Dihydroxy-6,7-dimethoxyxanthone (IIb) shows the same oxygenation pattern as celebixanthone (III),[11] while 1,6-dihydroxy-7,8-methylenedioxyxanthone (I) belongs to a hitherto undescribed type of oxygenated natural xanthones. 1,3-Dihydroxy-2,8-dimethoxyxanthone, a further representative of this type, was recently isolated from a *Kielmeyera* species.[12]

EXPERIMENTAL

For experimental techniques see Ref. 5. All known compounds were identified by direct comparison with authentic samples.

Isolation of the constituents. Ground wood (7·5 kg) and bark (2·5 kg) of *C. densiflora* were extracted separately first with hot benzene and next with hot EtOH. The benzene extract of the wood (12 g) was chromatographed on silica using successively light petroleum (A_1), benzene (A_2), benzene–$CHCl_3$ (1:1) (A_3) and $CHCl_3$ (A_4). The EtOH extract of the wood (5 g) was chromatographed on silica using successively benzene (B_1), benzene–$CHCl_3$ (5:1) (B_2,) benzene–$CHCl_3$ (1:1) (B_3) and $CHCl_3$ (B_4). The benzene extract of the bark (5 g) was chromatographed on silica using successively light petroleum–benzene 1:1 (C_1), benzene (C_2) and $CHCl_3$ (C_3). Ground wood (10 kg) of *C. grandifolia* was extracted successively with hot benzene and hot EtOH. The benzene extract (20 g) was chromatographed on silica using successively benzene (D_1), benzene–$CHCl_3$ (5:1) (D_2), benzene–$CHCl_3$ (2:1) (D_3), benzene–$CHCl_3$ (1:1) (D_4) and $CHCl_3$ (D_5). The EtOH extract was chromatographed on silica using successively benzene–$CHCl_3$ (5:1) (E_1), benzene–$CHCl_3$ (2:1) (E_2), benzene-$CHCl_3$ (1:1) (E_3) and $CHCl_3$ (E_4). A_1 gave aliphatic material which was not further examined. A_2, D_3 and E_2 were recrystallized from light petroleum giving sitosterol. A_3 and B_3 were recrystallized from EtOH giving IIb (25 mg). B_4 was crystallized fractionally from $CHCl_3$, yielding initially I (1·5 mg) and subsequently betulinic acid. A_4, D_5 and E_4 were recrystallized from EtOH giving betulinic acid. B_1, C_2, D_2 and E_1 were recrystallized from EtOH giving lupeol. B_2, D_4 and E_3, were purified by sublimation giving vanillin. C_1 was crystallized from light petroleum–benzene (1:1) giving friedelin. D_1 was washed with hexane giving lupenone. From C_3 nothing useful could be isolated.

1,5-*Dihydroxy*-6,7-*dimethoxyxanthone* (IIb) was obtained as yellow needles, m.p. 249–251°. λ_{max}^{EtOH}(nm): 236, 260, 315, 379 (ϵ 19 600, 32 600, 11 000, 6400), $\lambda_{max}^{EtOH+NaOH}$ (nm): 264, 285sh, 351 (ϵ 30 500,11 800, 9200), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 249, 265sh, 351 (ϵ 26 400, 22 200, 10 700), $\lambda_{max}^{EtOH+AlCl_3}$(nm):235,267,286,324, ($\epsilon$ 23 500, 27 200, 18 600, 11 100). Gibbs test, λ_{max} (nm): 450, 680 (Absorbance 0·72, 0·83). ν_{max}^{KBr} (cm^{-1}): 3280, 1640, 1600, 1582, 1125, 799. NMR ($F_3C{\cdot}CO_2H$, τ): 2·13 (*t*, *J* 8·5 Hz, H-3), 2·59 (*s*, H-8), 2·68 (*q*, *J* 8·5 and 1·5 Hz, H-4), 2·94 (*q*, *J* 8·5 and 1·5 Hz, H-2), 5·76 (*s*, $OC\underline{H}_3$), 5·93 (*s*, $OC\underline{H}_3$). MS: M, Found: 288·0641; $C_{15}H_{12}O_6$ requires: 288·0634. M 288 (100%), *m/e* (%) 273 (10), 258 (19), 245 (8), 243 (11), 230 (10), 227 (13), 215 (6), 201 (5), 200 (5), 199 (9), 187 (5), 173 (6), 144 (9).

1,5-*Diacetoxy*-6,7-*dimethoxyxanthone* was obtained from IIb as needles, m.p. 139–141°. λ_{max}^{EtOH} (nm): 241, 250sh, 276, 303, 356 (ϵ 26 900, 24 800, 9100, 6700, 6600).

1,5,6,7-*Tetramethoxyxanthone* (IIa) was obtained from IIb as crystals, m.p.158–159°. λ_{max}^{EtOH} (nm): 245sh, 253, 265sh, 292, 364 (ϵ 33 000, 41 000, 19 000, 14 200, 11 000); NMR ($CDCl_3$, τ): 2·39 (*q*, *J* 8 and 8·5 Hz, H-3), 2·48 (*s*, H-8), 2·88 (*q*, *J* 8·5 and 1·5 Hz, H-4), 3·19 (*q*, *J* 8 and 1 Hz, H-2), 5·93 (*s*, $OC\underline{H}_3$), 5·97 (*s*, $OC\underline{H}_3$), 5·99 (*s*, $OC\underline{H}_3$), 6·05 (*s*, $OC\underline{H}_3$).

1,6-*Dihydroxy*-7,8-*methylenedioxyxanthone* (I) was obtained as yellow rectangular plates, m.p. 318–320°. λ_{max}^{EtOH}(nm): 229, 254, 322, 361 (ϵ 31 000, 38 000, 12 300, 11 000), $\lambda_{max}^{EtOH+NaOH}$ (nm): 246, 260, 289, 351 (ϵ 34 000, 32 200, 14 200, 12 000), $\lambda_{max}^{EtOH+NaOAc}$ (nm): 231, 250, 275sh, 356 (ϵ 29 200, 34 500, 20 200, 16 400), $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 234, 258, 287, 339 (ϵ 33 600, 28 200, 16 200, 16 300). ν_{max}^{KBr} (cm^{-1}): 3226, 1647, 1626, 1597, 1092, 1075, 947, 808. Gibbs test, λ_{max} (nm): 430, 675 (Absorbance resp. 0·36, 1·03). MS: M, Found: 272·0315; $C_{14}H_8O_6$ requires: 272·0321. M 272 (100%), *m/e* (%) 271 (8), 256 (23), 242 (6), 187 (6), 158 (5), 136 (10), 135 (6), 130 (6), 129 (6), 123 (6), 114 (6), 102 (10), 101 (6).

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