

TWO NEW C-PRENYLATED DERIVATIVES OF 2,4-DIHYDROXY
BENZOIC ACID FROM *LONCHOCARPUS NICOU* ROOTS

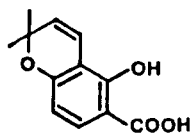
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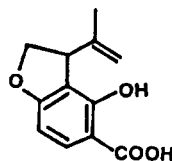
A previous study on *Lonchocarpus nicou* Benth. (Leguminosae) roots has yielded prenylated polyphenols from the *n*-hexane extract: six rotenoids, the isoflavone **5**, and the stilbene **3** (1). In continuation of this work, the CHCl₃ extract has been examined, and during fractionation, two minor constituents have been detected. The isolation and the structure elucidation of the new natural products **1** and **2** are reported here.

Compound **1**, amorphous, C₁₂H₁₂O₄, [M]⁺ *m/z* 220, is characterized by a blue fluorescence. The ¹H-nmr spectrum run in CDCl₃ (Table 1) indicated two parts in this molecule: (a) a 1,2,3,4-tetrasubstituted aromatic ring (δ 7.67 and 6.37, H-6 and H-5) and (b) a dimethylpyran

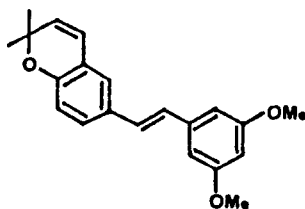
(δ 6.71, 5.59, and 1.47, H-4', H-3', H-7', and H-8'). The low-field region of the ¹³C-nmr spectrum showed three signals corresponding to a carbonyl function (δ 172.96, C-7) and to two ethylenic *O*-bound carbons (δ 167.98 and 158.90, C-4 and C-2). The bathochromic uv shifts obtained with AlCl₃ indicated a chelated hydroxyl. A comparative analysis of the δ values relative to the ethylenic proton vicinal to the aromatic ring in the dimethylpyran polyphenols **1** and **3-7** (Table 2) convincingly supported the proposed structure for compound **1**, in which the involved proton (δ 6.71) has to be close to an oxygen atom as in lonchocarpusone [5], deguelin [6], and hydroxydeguelin



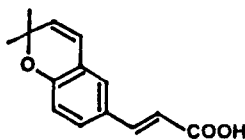
1



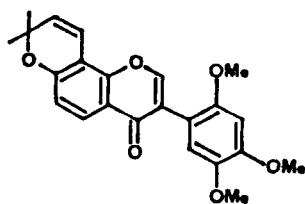
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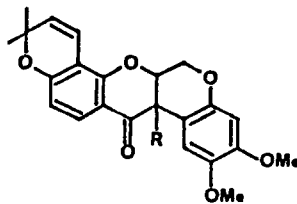
6 R=H
7 R=OH

TABLE 1. ¹H-nmr Data of Compounds **1** and **2**.^a

Proton	Compound	
	1	2
H-5	6.37, d, <i>J</i> = 8.6 Hz	6.42, d, <i>J</i> = 8 Hz
H-6	7.67, d, <i>J</i> = 8.6 Hz	7.78, d, <i>J</i> = 8 Hz
H-2'		5.32, dd, <i>J</i> = 10, 7.5 Hz
		3.35, dd, <i>J</i> = 15.2, 10 Hz
H-3'	5.59, d, <i>J</i> = 10.1 Hz	3.00, dd, <i>J</i> = 15.2, 7.5 Hz
H-4'	6.71, d, <i>J</i> = 10.1 Hz	
		5.09, br s
H-7'	1.47, s	4.95, br s
H-8'	1.47, s	1.76, s

^a300 MHz, CDCl₃, δ ppm/TMS.

[7]. Compound **1** is, therefore, considered 2',2'-dimethylpyran(5',6':3,4)-2-hydroxybenzoic acid. The ¹³C-nmr spectrum was in agreement with ¹H-nmr data; C-1 (δ 104.0) was naturally shielded by the *para-O*-substitution as in 2,4-dihydroxybenzoic acid (δ 104.63) and contrary to that observed for 2,3-dihydroxybenzoic acid (δ 112.66) as reported in Table 3.

Compound **2** was less polar than **1**, but both had a similar blue fluorescence and molecular weight. The ¹H-nmr spectrum (Table 1) differed from that of **1** by the substitution of the dimethylpyran by an isopropenyl dihydrofuran (δ 5.32, 3.35, 3.00, 5.09, 4.95, 1.76, H-2', H-3', H-7', H-8'). As in compound **1**, the phenolic group and the carboxyl function were located at the same positions as shown by both the bathochromic uv shifts (AlCl₃) and the ¹³C-nmr peaks (δ 104.66, 159.57, 167.28, 173.20, C-

1, C-2, C-4, C-7). These data supported, therefore, the assignment of **2** as the new compound 2'-isopropenyl-2',3'-dihydrofuran(4',5':3,4)-2-hydroxybenzoic acid.

Prenylated phenolic acids so far are rare; metabolites of this kind and particularly *p*-coumaric acid derivatives are reported to be accumulated in some Compositae (2,3). The two phenolic acids **1** and **2** present in *L. nicou* roots seem to be the first examples of the prenylated benzoic acid group.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURE.—

The source of plant material was previously reported (1). Analytical tlc was carried out on Si gel 60F-254 plates (E. Merck) and polyamid-6 UV254 (Macherey Nagel). Si gel 60PF-254 containing gypsum (E. Merck) for preparative layer chromatography was used for centrifugal circular tlc (cctlc). Polyamide CC6 (Macherey Nagel) was used for cc. Uv spectra were measured in MeOH on a Beckman 25 spectrometer. ¹H- and ¹³C-nmr

TABLE 2. Comparative Analysis of δ-values Relative to the Ethylenic Proton Vicinal to the Aromatic Ring in the Dimethylpyran Polyphenols **1** and **3-7**.^a

Compound					
1	3	4^b	5	6	7
6.71	6.35	6.27	6.85	6.67	6.59

^a300 MHz, CDCl₃, δ ppm/TMS.^bValue for compound **4** was taken from Labbe *et al.* (3) (80 MHz).

TABLE 3. ^{13}C -nmr Chemical Shifts of Compounds **1**, **2**, 2,4-Dihydroxybenzoic Acid [**3**], and 2,3-Dihydroxybenzoic Acid [**4**].^a

Carbon	Compound			
	1	2	3 ^b	4 ^b
C-1	104.00	104.66	104.63	112.66
C-2	158.90	159.57	163.51 ^c	149.51
C-3	109.20	112.82	102.46	144.94
C-4	167.98	167.28	163.65 ^c	118.81
C-5	108.94	102.46	108.05	120.16
C-6	128.28	132.81	132.28	121.12
C-7	172.96	173.20	172.40	172.61
C-2'	77.60	87.87		
C-3'	115.89	31.18		
C-4'	131.37			
C-6'		143.32		
C-7'	28.29	112.49		
C-8'	28.29	17.02		

^a75.5 MHz, CDCl_3 , δ ppm/TMS.

^bCompounds **3** and **4** were dissolved in $\text{CDCl}_3 + \text{MeOH}$ (2 drops).

^cAssignments may be interchanged.

spectra (CDCl_3 ; δ ppm/TMS) were recorded on an AM300 Bruker nmr spectrometer. Ei mass spectra were taken on a Nermag 10-10C mass spectrometer (80 eV).

ISOLATION OF THE BENZOIC ACIDS.—*L. nicou* roots, first extracted at room temperature with *n*-hexane and then with C_6H_6 , were treated with CHCl_3 to afford a brown viscous mass. A portion (500 mg) of this extract was subjected to fractionation by cctlc on Si gel and was eluted with a solvent gradient from CHCl_3 to CHCl_3 -MeOH (70:30). Combination of similar eluates provided 20 fractions on the basis of tlc analysis using the systems Si gel; CHCl_3 -MeOH (95:5 and 85:15) and polyamide; C_6H_6 -MeOH (98:2 and 96:4). Fractions 7-11 (129 mg), containing compounds **1** and **2**, were treated by cctlc on Si gel and eluted by a solvent gradient from CHCl_3 to CHCl_3 -MeOH (85:15) providing eleven fractions. Benzoic acids **1** and **2** were present together in fractions 3 and 4 (35 mg). Separation of the two compounds was finally accomplished by polyamide cc with C_6H_6 -MeOH (95:5) as the eluting solvent. This procedure yielded 1.5 mg of each product.

2',2'-DIMETHYLPYRAN(5',6':3,4)-DIHYDROXYBENZOIC ACID [**1**].—White amorphous

powder; uv λ MeOH 325 sh, 302 sh, 285, 242; /NaOMe 324 sh, 311 sh, 286 sh, 240; /AlCl₃ 357 sh, 330 sh, 312 sh, 295, 255 nm; ms (80 eV) *m/z* (%) [M]⁺ 220 (24), 205 (28), 202 (2), 187 (100), 174 (4), 159 (6), 131 (5), 115 (3), 103 (5), 89 (4), 77 (10), 69 (8), 57 (10), 55 (12); ¹H nmr see Table 1; ¹³C nmr see Table 3.

2'-ISOPROPENYL-2',3'-DIHYDROFURAN(4',5':3,4)-DIHYDROXYBENZOIC ACID [**2**].—White amorphous powder; uv λ MeOH 292 sh, 256; /NaOMe 290, 253; /AlCl₃ 335 sh, 305 sh, 275 nm; ms (80 eV) *m/z* (%) [M]⁺ 220 (100), 205 (10), 187 (96), 185 (18), 174 (45), 161 (22), 160 (9), 159 (19), 146 (16), 131 (19), 115 (11), 105 (10), 95 (12), 77 (23), 69 (25), 57 (46), 55 (55); ¹H nmr see Table 1; ¹³C nmr see Table 3.

LITERATURE CITED

1. M. Kaouadji, A. Agban, A.-M. Mariotte, and M. Tissut, *J. Nat. Prod.*, **49**, 281 (1986).
2. F. Bohlman, C. Zdero, R.M. King, and H. Robinson, *Phytochemistry*, **23**, 1135 (1984).
3. C. Labbe, J. Roviroso, F. Faini, M. Mahu, A. San-Martin, and M. Castillo, *J. Nat. Prod.*, **49**, 517 (1986).

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