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TWO *C*-METHYL-*C*-PRENYLDIHYDROCHALCONES FROM *PLATANUS ACERIFOLIA*

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Key Word Index—*Platanus acerifolia*; Platanaceae; buds; *C*-methyl-*C*-prenyl-dihydrochalcones.

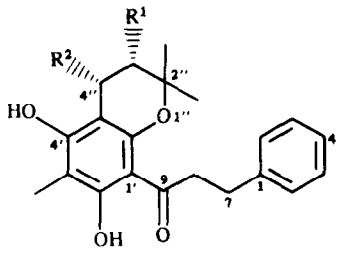
Abstract—Two novel dihydrochalcones were isolated from the buds of *Platanus acerifolia*. Separations were made by centrifugal TLC and HPLC and structure elucidation was achieved by UV, ^{1}H, ^{13}C NMR and MS spectra. The two related components are characterized by both *C*-methylation and *C*-prenylation.

INTRODUCTION

Platanus acerifolia Willd. (Platanaceae) has been the subject of previous phytochemical analysis identifying flavanones [1], 6′-oxo-dihydrochalcones [2, 3], and flavonols [4, 5]. All these flavonoids are *O*- or *C*-prenylated, several of them being also *C*-methylated. The benzene extract of the buds collected in September, has been analysed, and during fractionation, two new dihydrochalcones, **1** and **2**, have been isolated by centrifugal TLC and purified by HPLC.

RESULTS AND DISCUSSION

Compound **1**, $C_{21}H_{24}O_5$ $[M]^{+\cdot}$ *m/z* 356, exhibited two UV bands at λ287 and 342 nm; insensitive to aluminium trichloride in spite of a chelated hydroxyl (δ13.59), this molecule reacted with sodium acetate changing the UV spectrum into one broad band at λ325 nm. The mass spectrum showed fragment ions at *m/z* 77, 91, 105 and 251, indicating a dihydrochalcone skeleton with an unsubstituted B-ring. This partial structure was confirmed by ^{1}H NMR (δ7.36, 3.05 and 3.46, B-ring H, H-7 and H-8) (Table 1), as well as by ^{13}C NMR (δ142.1, 128.6, 128.5, 126.0, 30.4, 44.0, and 203.5, C-1, C-2, 6, C-3, 5, C-4, C-7, C-8, and C-9) (Table 2). The A-ring was totally substituted as indicated by the ^{13}C NMR spectrum for three ethylenic quaternary *O*-bound carbons (δ162.5, 161.2 and 158.3) and three ethylenic quaternary carbons (δ104.2, 103.2, and 101.3) bearing the above-mentioned C_6–C_3 partial structure, a methyl group, and a C_5-chain cyclized into a dihydrodimethylpyran (Tables 1 and 2). The downfield shift signals of the ethylenic quaternary *O*-bound carbons excluded any *ortho*-oxygenation so that ring A has a phloroglucinol oxygenation pattern. The substituents were consistent with two hydroxy groups (δ13.59 and 8.90, HO-6′ and HO-4′), and an oxygen included in the reported dihydrodimethylpyran. The bathochromic UV shift of 38 nm, obtained with sodium acetate for band II, convincingly supported the proposed structure **1** in which the 4′-position is hydroxylated. Finally the third OH-group (δ3.90) was identified with an alcoholic function located at the 4″-position (δ4.87). Thus, the new Compound is 5′,2″,2″-trimethyl-4′,6′,4″-trihydroxy-dihydropyran (5″, 6″:3′, 2′) dihydrochalcone.



1 R^1 = H, R^2 = OH
2 R^1 = OH, R^2 = H

Table 1. ^{1}H NMR data of components **1** and **2***

H	Components 1	2
B-ring	*ca* 7.36, *m*	*ca* 7.36, *m*
7	3.05, *t*, *J* = 8.5 Hz	3.07, *t*, *J* = 8.5 Hz
8	3.46, *br t*, *J* = 8.5 Hz	3.51, *br t*, *J* = 8.5 Hz
3″	3.19, *br t*, *J* = 8.7 Hz	3.87, *br t*, *J* = 6.7 Hz
4″	4.87, *t*, *J* = 8.7 Hz	under H_2O peak
Me-5′	2.06, *s*	2.10, *s*
Me-2″	1.27, *s*	1.37, *s*
	1.35, *s*	1.45, *s*
HO-4′	8.90, *br s*	8.50, *br s*
HO-6′	13.59, *s*	14.16, *s*
HO-4″	3.90, *br s*	4.47, *br s*

*At 300 MHz, acetone-d_6, δppm.

From the coupling value $J_{4'',3''a} = J_{4'',3''e} = 8.7$ Hz, the 4″-OH group clearly has an equatorial orientation [6]. As previously reported for the 6-*C*-methylflavanone strobopin [7], and for *C*-alkylated polyphenols with alkyl group *ortho* to the chelated hydroxyl [8], there is no aluminium-induced shift in the UV spectrum due to steric hindrance caused by Me-5′.

Table 2. ^{13}C NMR data of components **1** and **2***

C	Components 1	2
1	142.1	142.1
2, 6	128.6[a]	128.5
3, 5	128.5[a]	128.5
4	126.0	126.0
7	30.4	30.8
8	44.0	45.6
9	203.5	under acetone peak
1′	101.3	100.7
2′	158.3	160.1
3′	103.2	99.3
4′	162.5	163.1
5′	104.2	103.7
6′	161.2	162.0
2″	70.8	78.6
3″	27.1	68.4
4″	91.6	26.5
Me-5′	7.0	7.1
Me-2″	25.5	25.2
	25.5	20.1

*At 75.5 MHz, acetone-d_6, δppm.
[a]Signals may be interchanged.

Compound **2** was slightly more polar than **1** but had a similar M_r. Mass spectral as ^1H and ^{13}C NMR data also indicated a dihydrochalcone skeleton with unsubstituted B-ring and fully substituted A-ring. Compound **2** differed from **1** by a 3″-OH instead of a 4″-OH in **1**. This result was indicated by ^1H NMR signals (δ3.87, 2.60 and *ca* 2.90–3.10, H-3″ and H-4″) and ^{13}C NMR peaks (δ68.4 and 26.5, C-3″ and C-4″). As in **1**, the 4′-OH group is free; this is shown by the bathochromic UV shift of 40 nm for band II, in the presence of sodium acetate. Thus, the new compound is 5′,2″,2″-trimethyl-4′,6′,3″-trihydroxy-dihydropyran(5″,6″:3′,2′)dihydrochalcone. The equatorial orientation of the 3″-OH is in agreement with the coupling value $J_{3'',4''a} = J_{3'',4''e} = 6.7$ Hz [6].

In comparison with **2**, the chelation between the 4′-OH and the 4″-OH in **1** is responsible for the stability of this compound in solution, as well as for its less polar behaviour on TLC and HPLC. The supplementary heterocycle in **1** seems to enhance both the UV band II absorption (**1** λ342 nm, **2** λ335 nm) and the steric hindrance of the 6′-OH preventing the formation of an $AlCl_3$ complex. The ^1H NMR chemical shifts of the three OH-groups are also affected by this change; in **1**, HO-4′ displays a downfield shift (+0.40 ppm), while, on the opposite both HO-6′ and HO-4″ are shifted upfield by −0.57 ppm.

3″-Hydroxydihydropyran chalcones have been previously reported [9–11], but not 4″-hydroxy compounds. Compound **1** is the first representative of the second group. It is also the first report of a dihydrochalcone associated with hydroxylated dimethyldihydropyran as well as of dihydrochalcones involving both *C*-methylation and *C*-prenylation.

EXPERIMENTAL

Collection data were reported previously [2].

General. TLC was carried out on pre-coated silica gel 60F-254 plastic sheets (Merck). Separation by centrifugal TLC on silica gel used a Chromatotron apparatus (Harrison Research). Purification was performed by semi-preparative HPLC on a Waters model equipped with a 6000A pump, a variable wavelength detector and a Lichrosorb Si 60 column (5μm, 250 × 7 mm) (Merck). UV spectra were recorded with the usual shift reagents according to standard procedures [12, 13]. EI mass spectra were run at 80 eV. NMR spectra were measured, using the solvent signal as reference (Me_2CO-d_6: δ2.13 for ^1H and δ29.2 for ^{13}C).

Extraction and isolation of the dihydrochalcones. Fresh buds of *P. acerifolia* (102 g), were successively extracted at room temp. with *n*-hexane and then with C_6H_6. A part of the crude C_6H_6 extract (1.15 g) was submitted to centrifugal TLC on silica gel with *n*-hexane–C_6H_6 (2:3), C_6H_6 and increasing amounts of $CHCl_3$ in C_6H_6. The eluate was collected in 15 fractions. Compounds **1** and **2** were detected together in the first fractions by the use of TLC on silica gel with *n*-hexane–$CHCl_3$–*i*-PrOH–MeOH (34:4:1:1). Final purification was achieved by HPLC on Lichrosorb Si 60 with *n*-hexane–$CHCl_3$–*i*-PrOH–MeOH (36:2:1:1). This procedure yielded 5 mg of compound **1** and 3.5 mg of compound **2**.

Compound (**1**). White amorphous powder; UV λ_{max}^{MeOH} nm: 287, 342; unchanged with $AlCl_3$; (NaOAc) 287sh, 325; (NaOMe) 326. ^1H NMR: see Table 1. ^{13}C NMR: see Table 2.

Compound (**2**). White amorphous powder; UV λ_{max}^{MeOH} nm: 292, 335sh; ($AlCl_3$) 300, 350sh; unchanged with HCl; (NaOAc) 292sh, 332; (NaOMe) 333. ^1H NMR: see Table 1. ^{13}C NMR: see Table 2.

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