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# NEW PRENYLATED FLAVANONES FROM *PLATANUS ACERIFOLIA* BUDS

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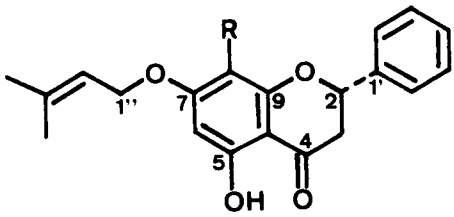
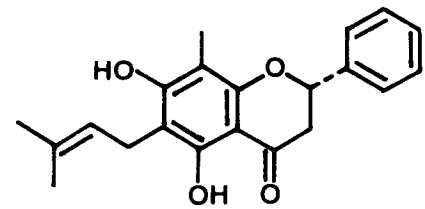
*Platanus acerifolia* Willd. (Platanaceae) buds contain *C*-substituted polyphenols (1, 2). The *n*-hexane extract has now yielded three apolar compounds, identified as flavanones **1, 2,** and **3**. Isolation was performed by use of repeated circular centrifugal tlc on silica gel eluted with a gradient of *n*-hexane/$CHCl_3$; purification of compounds **2** and **3** was carried out by crystallization from *n*-hexane.

Viscous, compound **1** was given the molecular formula $C_{20}H_{20}O_4$, $M^{+\cdot}$ *m/z* 324; its $^1$H-nmr spectrum ($CDCl_3$, 300 MHz) exhibited signals relative to: a dimethylallyl chain $(CH_3)_2C{=}CH\text{-}CH_2$ at δ 1.80 ppm (3H), d, $J$=1 Hz, δ 1.73 ppm (3H), broad s, δ 5.43 ppm (1H), dqq, $J$=6.5, 1, 1 Hz, δ 4.52 ppm (2H), broad d, $J$=6.5 Hz; a $>CH\text{-}CH_2$-chain at δ 5.40 ppm (1H), dd, $J$=12.5, 3 Hz, δ 3.08 ppm (1H), dd, $J$=17, 12.5 Hz, δ 2.81 ppm (1H), dd, $J$=17, 3 Hz; a 1,2,3,5-tetrasubstituted aromatic ring in which *meta*-related protons exhibited doublets ($J$ 2.5 Hz) at δ 6.08 and 6.06 ppm; a monosubstituted aromatic ring indicated by a multiplet integrating for 5H at δ ca. 7.43 ppm; and a chelated hydroxyl group recorded as a sharp singlet at δ 12.0 ppm. As indicated by the uv spectrum run in MeOH (λ 330 sh, 285 nm) and then in $AlCl_3$ (λ 370, 308 nm) not changed in HCl, the OH group was *ortho*-related to a carbonyl function appearing at δ 195.6 ppm in the $^{13}$C-nmr spectrum of the natural product. Besides this signal, the low field region of this spectrum displayed resonances at δ 167.3, 164.1, and 162.7 ppm corresponding to three quaternary ethylenic *O*-bound carbons, including the C-atom bearing the hydroxy group. From those results, it was established that the tetrasubstituted aromatic ring was 1,3,5-trioxygenated and was responsible for the fragment-ion at *m/z* 152. On the other hand, the mass spectrum showed another prominent peak at *m/z* 104 associating the monosubstituted aromatic ring and the $>CH\text{-}CH_2$-chain listed above. On the basis of deshielding affecting the methine (δ 5.40 ppm) owing to *O*-binding, this chain was deduced as being included in a γ-dihydropyrone ring along with the carbonyl function. This suggested a flavanone nucleus hydroxylated at C-5 and 7-*O*-substituted with the remaining dimethylallyl chain as indicated by deshielding of the methylene (δ 4.52 ppm) and the fragment-ion $(M\text{-}68)^{+\cdot}$ at *m/z* 256. Finally, the relative 2*S*-configuration was assigned to compound **1** on the basis of couplings recorded for H-2 ($J$=12.5, 3 Hz) showing this proton with the axial




**1** R=H
**2** R=Me




**3**

orientation. From these data, compound **1** was considered to be 5-hydroxy-7-*O*-prenylflavanone corresponding to 7-*O*-prenylpinocembrin. The $^{13}$C-nmr spectrum, in agreement with the proposed formula (see Experimental), displayed C-5 at δ 164.1 ppm, C-7 at δ 167.3 ppm, and C-9 at δ 162.7 ppm, in comparison with records in pinocembrin at δ 163.6, 166.6, and 162.7 ppm for C-5, 7, and 9, respectively (3). This compound has been reported but not described in the genus *Helichrysum* (4).

Compound **2** ($C_{21}H_{22}O_4$, $M^{+\cdot}$ *m/z* 338) showed a chromatographic behavior slightly more apolar than that of compound **1** and the same $^1$H-nmr spectrum with the exception of a supplementary methyl group (δ 2.03 ppm) instead of an aromatic proton on ring A of the flavanone nucleus. Localization of this methyl in the 8-position was simultaneously deduced from both the uv spectrum in the presence of $AlCl_3$ and the $^{13}$C-nmr data. Effectively, the bathochromic uv shifts induced by $AlCl_3$ (ΔλI 27 nm, ΔλII 22 nm) corresponded to those of a 5-hydroxy-8-*C*-methylflavanone (ΔλI 28 nm, ΔλII 19 nm), in contrast with those of a 5-hydroxy-6-*C* methylflavanone (ΔλI 15 nm, ΔλII 3 nm) (5). On the other hand, comparison with the $^{13}$C-nmr spectrum of **1**, the *C*-methylation in **2** would have to produce the same shielding on the *ortho* C-atoms, this effect being increased on the *para* C-atom (6). On the basis of this property and the recorded δ-values 165.3, 161.1, 160.6 ppm and taking into account that C-7 is more deshielded than C-5 and C-9, consequent to the *para*-position to the carbonyl group, then only the 8-*C*-methyl possibility was retained parallel to the remaining assignments 161.1 ppm (C-5) and 160.6 ppm (C-9). Compound **2** which also displayed a 7-*O*-di methylallyl chain, as indicated by the $^1$H- and $^{13}$C-nmr data (see Experimental), was therefore identified as 5-hydroxy-7-*O*-prenyl-8-*C*-methylflavanone, corresponding to 7-*O*-prenyl-8-*C*-methylpinocembrin. This natural product is reported here for the first time.

Compound **3**, more polar but less concentrated than **1** and **2** in the *n*-hexane extract of *P. acerifolia* buds, was also a flavanone, as indicated by the $^1$H-nmr data relative to the Ar-CH(O)-$CH_2$-CO- chain at δ 5.40, 3.05, and 2.85 ppm, including an unsubstituted B-ring recorded as a multiplet at δ ca. 7.48 ppm. This compound showed the same molecular formula $C_{21}H_{22}O_4$ $M^{+\cdot}$ *m/z* 338 as compound **2**, and the $^1$H-nmr spectrum also exhibited signals connected with a *C*-Me (δ 2.05 ppm) and a dimethylallyl group (δ 5.22, 3.37, 1.79, and 1.75 ppm). In this case, the chain was *C*-bound as supported by the δ-value of the methylene at 3.37 ppm instead of 4.55 ppm in **2** and the 7-hydroxyl was free, explaining the polarity of such a compound in comparison with **1** and **2**. The uv bathochromic shifts recorded in the presence of $AlCl_3$ and not changed by HCl simultaneously suggested that the 5-hydroxyl was free and that the methyl group was located at C-8, giving ΔλI 35 nm and ΔλII 20 nm. These data are in agreement with 5-hydroxy-8-*C*-methylflavanone (5). Consequently, compound **3** was considered to be 5,7-dihydroxy-6-*C*-prenyl-8-*C*-methylflavanone corresponding to 6-*C*-prenyl-8-*C*-methylpinocembrin, a new natural product.

*P. acerifolia* is a species characterized now by a diversified polyphenolic metabolism where *O*- or *C*-prenylation is always present and sometimes associated with *C*-methylation. Considered individually, *C*-methylation and *C*-prenylation are substitution patterns relatively more common in the flavonoids in contradistinction to *O*-prenylation which is more restricted in its occurrence (7). Compounds **2** and **3** are the only examples of flavonoids showing both *C*-methylation and *C*- or *O*-prenylation.

## EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—

The source of plant material and general extraction were previously reported (2). Uv spectra were recorded in MeOH on a Beckman 25 spectrometer. $^1$H- and $^{13}$C-nmr spectra were measured on an AM300 Brucker nmr spectrometer ($CDCl_3$, δ ppm/TMS). Ei mass spectra were taken on an AEI MS902 mass spectrometer. Mp were obtained from a capillary melting point Büchi apparatus and were uncorrected. Silica gel 60 PF-254 containing gypsum for preparative layer chromatography, purchased from E. Merck, was used for circular centrifugal thin layer chromatography (cctlc).

ISOLATION OF THE FLAVANONES.—After isolation of grenoblone from the *n*-hexane extract of *P. acerifolia* buds by cctlc (2), the next four polar fractions were subjected to a similar procedure to yield flavanones **1, 2,** and **3**. The two first fractions (15 mg) were treated by cctlc in using *n*-hexane-$CHCl_3$ (98:2) to isolate compound **2** which was further purified by repeated crystallization in *n*-hexane to give colorless needles (3.7 mg). The third fraction (22 mg) was also subjected to cctlc on silica gel (*n*-hexane-$CHCl_3$, 95:5) to afford compound **1** as an oil (12 mg). Fraction 4 (6 mg) was finally also chromatographed by cctlc on silica gel (*n*-hexane-iPrOH, 95:5) to yield compound **3** which crystallized from *n*-hexane as colorless needles (1.5 mg).

7-*O*-PRENYLPINOCEMBRIN (**1**).—Oil; uv λ MeOH 330 sh, 285, 227 sh, 214; /$AlCl_3$=/$AlCl_3$+HCl 370, 308, 222, 207 sh; /NaOMe 350, 285, 242 sh, 215 nm; ms (70 eV) *m/z* (%) 324 ($M^{+\cdot}$, 53), 309 (3), 281 (2), 269 (2.5), 256 (98), 238 (15), 228 (6), 213 (3), 179 (100), 165 (2), 152 (70), 124 (30), 123 (32), 104 (41), 103 (25), 97 (12), 95 (6), 91 (14), 87 (12), 85 (70), 83 (66), 78 (15), 77 (18), 69 (98); $^1$H nmr (300 MHz, $CDCl_3$) δ 12.0 (1H, s, HO-5), ca. 7.43 (5H, m, ArH), 6.08 (1H, d, $J$=2.5 Hz, H-6 or 8), 6.06 (1H, d, $J$=2.5 Hz, H-6 or 8), 5.43 (1H, dqq, $J$=6.5, 1, 1Hz, H-2″), 5.40 (1H, dd, $J$=12.5, 3 Hz, H-2), 4.52 (2H, broad d, $J$=6.5 Hz, H-1″), 3.08 (1H, dd, $J$=17, 12.5 Hz, $H_a$-3), 2.81 (1H, $J$=17, 3 Hz, $H_b$-3), 1.80 (3H, d, $J$=1 Hz, Me-3″), 1.73 (3H, broad s, Me-3″); $^{13}$C nmr (75.5 MHz, $CDCl_3$) δ 195.6 (C-4), 167.3 (C-7), 164.1 (C-5), 162.7 (C-9), 139.1 (C-3″), 138.4 (C-1′), 128.8 (C-3′, 4′, 5′), 126.1 (C-2′, 6′), 118.6 (C-2″), 103.0 (C-10), 95.7 (C-6), 94.8 (C-8), 79.2 (C-2), 65.3 (C-1″), 43.4 (C-3), 25.7 (Me-3″), 18.2 (Me-3″).

8-*C*-METHYL-7-*O*-PRENYLPINOCEMBRIN (**2**).—Colorless needles mp 98-100°; uv λ MeOH 335 sh, 290, 226 sh, 212; /$AlCl_3$=/$AlCl_3$+HCl 362, 312, 223 sh, 210 nm; /NaOMe=/MeOH; ms (70 eV) *m/z* (%) 338 ($M^{+\cdot}$, 17), 323 (1.5), 304 (2), 295 (1.5), 270 (100), 252 (2), 193 (31), 166 (24), 138 (25), 137 (27), 131 (2.5), 115 (2), 110 (5), 104 (23), 103 (22), 91 (8), 78 (13), 77 (17), 69 (79); $^1$H nmr (300 MHz, $CDCl_3$) δ ca. 7.48 (5H, m, ArH), 6.10 (1H, s, H-6), 5.45 (1H, dqq, $J$=6.5, 1, 1 Hz, H-2″), 5.41 (1H, dd, $J$=12.5, 3 Hz, H-2), 4.55 (2H, broad d, $J$=6.5 Hz, H-1″), 3.11 (1H, dd, $J$=17, 12.5 Hz, $H_a$-3), 2.82 (1H, dd, $J$=17, 3 Hz, $H_b$-3), 2.03 (3H, s, Me-8), 1.80 (3H, d, $J$=1 Hz, Me-3″), 1.73 (3H, broad s, Me-3″); $^{13}$C nmr (75.5 MHz, $CDCl_3$) δ 195.8 (C-4), 165.3 (C-7), 161.1 (C-5), 160.6 (C-9), 138.7 (C-3″), 138.4 (C-1′), 128.9 (C-3′, 4′, 5′), 126.2 (C-2′, 6′), 119.1 (C-2″), 106.4 (C-8), 102.8 (C-10), 91.8 (C-6), 79.4 (C-2), 65.5 (C-1″), 43.6 (C-3), 25.7 (Me-3″), 18.2 (Me-3″), 7.0 (Me-8).

6-*C*-PRENYL-8-*C*-METHYLPINOCEMBRIN (**3**).—Colorless needles mp 156-158°; uv λ MeOH 340 sh, 295, 235 sh, 218; /$AlCl_3$=/$AlCl_3$+HCl 375, 315, 225; /NaOMe 340, 290, 250 sh, 218 nm; ms (70 eV) *m/z* (%) 338 ($M^{+\cdot}$, 90), 323 (35), 321 (3.5), 309 (2.5), 305 (5), 295 (20), 283 (50), 270 (28), 260 (13), 256 (18), 234 (23), 233 (20), 219 (90), 206 (45), 191 (75), 179 (100), 166 (18), 131 (8), 123 (2.5), 109 (2.5), 104 (13), 103 (10), 91 (7), 83 (10), 69 (5); $^1$H nmr (300 MHz, $CDCl_3$) δ 12.29 (1H, s, HO-5), ca. 7.48 (5H, m, ArH), 5.40 (1H, dd, $J$=12.5, 3 Hz, H-2), 5.22 (1H, dqq, $J$=7, 1, 1 Hz, H-2″), 3.37 (2H, broad d, $J$=7 Hz, H-1″), 3.05 (1H, dd, $J$=17, 12.5 Hz, $H_a$-3), 2.85 (1H, dd, $J$=17, 3 Hz, $H_b$-3), 2.05 (3H, Me-8), 1.79 (3H, broad s, Me-3″), 1.75 (3H, broad s, Me-3″).

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