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IRIDOID AND PHENYLPROPANOID GLUCOSIDES FROM *TECOMA CAPENSIS*

MARCELLA GUISO,* CAROLINA MARRA, FRANCESCO PICCIONI and MARCELLO NICOLETTI†

Dipartimento di Chimica and †Dipartimento di Biologia Vegetale, Università 'La Sapienza', P.le A. Moro, 5, I–00185 Rome, Italy

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Key Word Index—*Tecoma capensis*; Bignoniaceae; iridoids; cornoside; rengioside B; halleridone; 7-*O*-(*p*-methoxy) benzoyl tecomoside.

Abstract—Leaves of *Tecoma capensis* contain, together with tecomoside, large quantities of it's benzoic and cinnamic esters. A novel glucoside was isolated and, by spectroscopic and chemical data, characterized as 7-*O*-(*p*-methoxy) benzoyl tecomoside. Flowers of *T. capensis* contain only tecomoside, together with two phenylethanoid-derived glucosides, cornoside and it's rearranged aglycone, halleridone, and rengioside B.

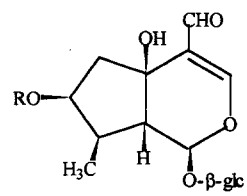
INTRODUCTION

Tecoma capensis is a creeper common to the tropical zone. It is grown as an ornamental plant in gardens of the Riviera Ligure, in the middle and south of Italy, where it flowers but rarely reaches the size typical of its species. Some iridoids, tecomoside (**1**) [1] and its four 7-*O*-acyl derivatives, (**2–5**) [2] previously have been isolated from ethanolic extracts of its leaves. Here we report a comparison between the glycosidic fractions obtained from the leaves and flowers.

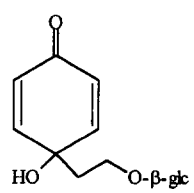
RESULTS AND DISCUSSION

Ethanolic extracts of the leaves were worked-up as previously described [2] yielding, in addition tecomoside (**1**) and its four 7-*O*-acyl derivatives [cinnamoyl (**2**), (*p*-methoxy)cinnamoyl (**3**), (*p*-hydroxy)cinnamoyl (**4**) and (*p*-hydroxy)benzoyl (**5**)], a novel iridoid glucoside, 7-*O*-(*p*-methoxy)benzoyl tecomoside (**6**). This compound, which is present in small amounts, shows chromatographic behaviour very similar to that of **3**. Separation of **6** was achieved by HPLC as previously reported [2].

The ^{1}H NMR spectrum of **6** appeared very similar to that of **3**, except in the zone between 6 and 8 ppm, where the signals of the aromatic protons of the *p*-methoxybenzoyl moiety appeared (AA′BB′-system with doublet-like signals centred at δ 7.69 and δ 6.89) instead of those arising from the *p*-methoxycinnamoyl moiety present in **3**. The different acylation pattern did not affect, as already noted, the chemical shifts of the other iridoid protons, the principal difference lying in the chemical shift of the methyl group at C-8 (*d*, 1.12 ppm in **3**; *d*, 1.00 ppm in **6**; both with a coupling constant of 6.7 Hz). Similar behaviour has been noted in the comparison between the ^{1}H NMR spectra of 7-*O*-(*p*-hydroxy)cynnamoyl tecomoside (**4**) and 7-*O*-(*p*-hydroxy)benzoyl tecomoside (**5**). The ^{13}C NMR spectrum of **6** supported the proposed structure. It shows (see Experimental) the characteristic signals of benzoyl and glucose moieties, as well as those of the



1 R = H
2 R = cinnamoyl
3 R = (*p*-OCH$_3$)cinnamoyl
4 R = (*p*-OH)cinnamoyl
5 R = (*p*-OH)benzoyl
6 R = (*p*-OCH$_3$)benzoyl



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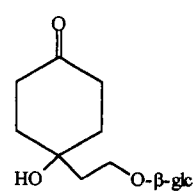

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* Author to whom correspondence should be addressed.

aglyconic part of tecomoside (**1**), with the signal of C-7 deshielded by benzoylation of the secondary hydroxyl function.

Conversely, the flower extract, contained only small amounts of **1**, while its 7-*O*-acyl derivatives were not detectable. The glucosidic fraction of these extracts showed the presence of cornoside (**7**) [3, 4] and of its 2,3,5,6-tetrahydroderivative, rengioside B (**8**) [5]. The nonglycosidic fraction contained the non-natural, rearranged aglucone of **7**, halleridone [4]. The identification of these three compounds was achieved by ^1H and ^{13}C NMR, while hydrogenation of **7** on Pd/C definitively confirmed the correlation between **7** and **8**.

It is interesting to note that, in many species of the Bignoniaceae, the presence of several cynnamoyl and benzoyl esters of the same iridoid glucoside is very common, while in other plant families, the presence in the same plant of iridoids with different substitution pattern is more common. It is also noteworthy that iridoids with the unusual C-11 aldehyde function are also often present in the Bignoniaceae.

EXPERIMENTAL

General. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AM 500 and Varian XL-300 spectrometers; chemical shifts are in ppm units from TMS; coupling constants in Hz. TLC: silica gel SiF_{254} (Merck). PC: Schleider & Schull N° 2043b MgI. Spray reagents: 2 N H_2SO_4, Vanillin (3 g vanillin, 4 ml conc. HCl, 100 ml MeOH) and resorcinol (5 g resorcinol, 4 ml conc. H_2SO_4, 300 ml EtOH).

Extraction and isolation of leaves. Extraction and isolation of the iridoid fr. from *T. capensis* Lindl leaves was performed as previously described [2]. Fr. A was chromatographed by semiprep. HPLC μ-Bondapack C-18 column (30 cm × 1/4 inch, particle size 10 μm) eluting with a MeOH–H_2O gradient. Compound **6** was eluted after compounds **2** and **3**.

7-O-(p-*Methoxy*)*benzoyl tecomoside*, **6**. Amorphous solid. $[\alpha]_D = -62.5$ (MeOH, *c* 0,1). IR ν_{max}^{KBr}: 3440, 1700, 1650, 1420, cm^{-1}. UV λ_{max}^{MeOH} 260 (log ε 4.2). ^1H NMR (MeOD): δ 9.27 (1 H, *s*, H-11), 7.69 and 6.89 (aromatic *p*-disubstituted system), 7.35 (1 H, *s*, H-3), 5.81 (1 H, *bs*, H-1), 4.61 (1 H, *d*, $J = 7.5$ Hz, H-1′), 3.83 (3 H, *s*, OCH_3), 2.64 (1 H, *dd*, $J = 15.8$ and 5.9 Hz, H-6_a), 2.25 (1 H, *dd*, $J = 15.8$ and 2.2 Hz, H-6_b), 5.09 (1 H, *m*, H-7), 2.33 (1 H, *d*, $J = 12.6$, H-9), 1.89 (1 H, *m*, H-8), 1.00 (3H, *d*, $J = 6.7$ Hz, H_3-10). ^{13}C NMR (MeOD): δ 13.0, C-10; 39.8, C-8; 46.9, C-6; 55.2, C-9; 55.9, OCH_3; 62.6, C-6′; 71.5, C-5 and C-4′; 74.4, C-2′; 76.8, C-7; 77.5, C-5′; 78.6, C-3′; 96.3, C-1; 100.2, C-1′; 126.6, C-4; 162.7, C-3; 128.3, C-1″; 133.3, C-2″ and C-6″; 116.2, C-3″ and C-5″; 163.2, C-4″; 168.6, COO; 192.6, C-11. FAB-MS *m/z*: $[M+Na]^+$ 533, $[M+K]^+$ 549.

Extraction and isolation of flowers. Fresh flowers (200 g) were extracted exhaustively with EtOH at room temp. The EtOH extract was concd to an aq. suspension, which was worked-up using the charcoal method. The aq. suspension was treated with charcoal powder (50 g) until it gave a negative vanillin test. The resulting suspension was stratified on a Gooch funnel. Elution with H_2O and H_2O–EtOH (9:1) removed salts and sugars (resorcinol test), whereas 20, 30, 50, 70 and 95% EtOH eluted glycoside-containing frs. The 50 and 70% EtOH frs were collected together (250 mg) and chromatographed on silica gel in *n*-BuOH-satd H_2O, yielded pure halleridone (11 mg), cornoside (**7**) (27 mg), rengioside B (**8**) (35 mg) and, finally, tecomoside (**1**) (16 mg), all as amorphous powders. The 20% and 30% EtOH frs were collected together (210 mg) and chromatographed as before, yielding pure halleridone, (3 mg), **7** (10 mg), **8** (15 mg) and, finally, **1** (35 mg).

Rengioside B, (**8**). Amorphous solid $[\alpha]_D = -20.0$ (MeOH, *c* 0,1). IR, ν_{max}^{KBr}: 3341, 2942, 2898, 1700, 1606, 1421, 1377, 1254, 1075, 1042, 941 cm^{-1}. UV, λ_{max}^{MeOH} 264 (log ε 3.3). ^1H NMR (500 MHz, CD_3OD): δ-aglycone 4.15 (1 H, *dt*, $J = 11.0$ and 8.0 Hz, H-2″a), 3.86 (1 H, *dt*, $J = 11.0$ and 8.0 Hz, H-2″b), 2.68 (2 H, *ddd*, $J = 16.0$, 10.5, 5.0, H-2ax, H-6ax), 2.31 (2 H, *dt*, $J = 16.0$ and 10.5 Hz, H-2eq, H-6eq), 2.03 (2 H, *ddd*, $J = 16.0$, 10.5 and 5.0 Hz, H-3ax, H-5ax), 1.97 (2 H, *t*, $J = 8.0$ Hz, H-1″), 1.94 (2 H, *dt*, $J = 16.0$ and 10.5 Hz, H-3eq, H-5eq); glucose 4.49 (1 H, *d*, $J = 8.0$ Hz, H-1′), 3.92 (1 H, *dd*, $J = 12.2$ and 2.4 Hz, H-6′a), 3.71 (1 H, *dd*, $J = 12.2$ and 6.4 Hz, H-6′b), 3.49 (1 H, *t*, $J = 9.2$ Hz, H-3′), 3.47 (1 H, *ddd*, $J = 9.2$, 6.4 and 2.4 Hz, H-5′), 3.38 (1 H, *t*, $J = 9.2$ Hz, H-4′), 3.25 (1 H, *dd*, $J = 9.2$ and 8.0 Hz, H-2′). ^{13}C NMR (125 MHz, D_2O): δ 219.5 (C-1), 103.0 (C-1′), 76.7* (C-3′), 76.5* (C-5′), 73.8 (C-2′), 70.5 (C-4), 70.4 (C-4′), 67.1 (C-2″), 61.5 (C-6′), 40.6 (C-1″), 37.1** (C-2, C-6), 36.5** (C-3, C-5);* and ** indicate assignments that can be reversed.

Cornoside (**2**). ^{13}C NMR (125 MHz, D_2O): δ 189.7 (C-1), 154.2 (C-3, C-5), 128.0 (C-2, C-6), 102.9 (C-1′), 76.6* (C-3′), 76.5* (C-5′), 73.8 (C-2′), 70.3 (C-4′), 69.1 (C-4), 65.7 (C-2″), 61.4 (C-6′), 39.1 (C-1″).

Catalytic hydrogenation of **7**. Cornoside (**7**) (20 mg), dissolved in EtOH (3 ml), was added to a suspension of 10 mg of Pd/C in 2 ml of EtOH, previously saturated with H_2 and left under H_2 for 3 hr. Catalyst was removed by filtration and the resulting soln evapd *in vacuo*, yielding 20 mg of a pure compound, identical to natural rengioside B (**8**).

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