CONSTITUENTS FROM THE LEAVES OF
LANTANA CAMARA (IV)

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Eight triterpenoids, betulonic acid (3), betulinic acid (4), oleanolic acid (5), lantadene A (6),
lantadene B (7), icterogenin (8), lantanolic acid (9), and ursolic acid (10), three flavonoids,
hispidulin (11), pectolinarigenin (12), and pectolinarin (13), as well as β-sitosteryl-3-O-β-D-
glucoside (2) and a mixture of campesterol (1a), stigmasterol (1b), and β-sitosterol (1c) were
isolated from the leaves of the yellow flowering taxa of Lantana camara L. The structures of
these compounds were established by spectroscopic methods and 2D NMR techniques.

Key words: Lantana camara L, Yellow flowering taxa, Triterpenoid, Flavonoid.

INTRODUCTION

Lantana camara L. (Verbenaceae) is a rambling shrub with a number of flower colors viz. red, pink, white,
yellow and violet¹. These plants are cultivated as ornamental or hedge plants in Taiwan².

Previously, we reported the phytochemical studies on the stems from the red, pink and yellow flowering taxa
of L. camara L³-⁵. Herein, we report the isolation of thirteen compounds from the leaves of yellow flowering taxa
of this plant, collected at Taichung, Taiwan.

RESULTS AND DISCUSSION

Compounds 1-13 were isolated from the ethyl acetate extract of the leaves of this plant as described in the
experimental section. Compound 1 was identified as a mixture of campesterol (1a), stigmasterol (1b) and β-
sitosterol (1c) by spectroscopic method and GC analysis⁴. Compound 2 was identified as β-sitosteryl-3-O-β-D-
glucoside by spectroscopic and chemical methods⁵. In addition, betulonic acid (3)⁴, betulinic acid (4)⁴, oleanolic

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Acid (5), lantadene A (6), lantadene B (7), icterogenin (8), lantanilic acid (9), ursolic acid (10), and hispidulin (11) were also identified by comparing their spectral data with those in literature.

Compound 12, obtained as yellow needles, mp: 210-211 °C, gave positive ferric chloride and Mg-HCl tests suggesting the presence of a flavonoid skeleton. It showed an ion peak at m/z 315 ([M + 1]⁺) which was 14 mass units more than hispidulin (11) in the FABMS spectrum. The UV spectral behavior of 12 with diagnostic reagents like NaOAc and AlCl₃ indicated the presence of the free 5- and 7-hydroxy groups. Comparison of C-6 (δ 131.05) and C-8 (δ 94.05) chemical shifts in the ¹³C NMR spectrum of 12 with those (C-6, δ 131.11 and C-8, δ 94.05) of 11 showed the presence of 6-methoxy group. The ¹H NMR spectrum showed an A₂X₂ system at δ 6.94 and 7.77 (each 2H, J = 9.0 Hz) due to a 4’-oxygenated B ring. The attachment of methoxyl group to C-4’- was confirmed by the correlation between H-3’ and a methoxyl signal at δ 3.81 and between H-2’ and H-3 in the NOESY spectrum. Furthermore, the HMBC spectrum indicated the correlations of H-3/C-2, C-4, C-1’, H-8/C-6, C-7, C-9, C-10, and 6-OCH₃ (δ 3.86)/C-6. Thus, 12 was deduced as pectolinarigenin and also confirmed by comparison of these data with those in the literature.

Compound 13, obtained as a yellow needle, mp > 300 °C, also gave positive ferric chloride and Mg-HCl tests. It possessed an ion peak at m/z 623 ([M + 1]⁺) in FABMS spectrum. The NMR signals of 13 were similar to...
The only difference was the appearance of two additional glycosyl signals. Two anomic protons [δ 5.26 (1H, br s, rhamnosyl H-1) and 5.63 (1H, d, J = 7.3 Hz, glucosyl H-1)] together with signals at δ 3.60 (1H, dd, J = 11.5, 4.9 Hz, glucosyl H-a-6), 3.75 (1H, dd, J = 11.5, 2.5 Hz, glucosyl H-b-6) and 1.18 (3H, d, J = 6.3 Hz, rhamnosyl H-6) revealed the rutinosyl moiety. The position of rutinosyl moiety on C-7 was confirmed by the HMBC correlation between glucosyl H-1 (δ 5.63) and C-7 (δ 157.7). Acid hydrolysis of 13 yielded an aglycone pectolinarigenin (12), D-glucose and L-rhamnose which were identified by the 1H NMR and thin-layer chromatography. According to the coupling constant, the configuration of D-glucose and L-rhamnose was determined as β- and α-linkage, respectively. The 13C NMR data of 13 also supported the attachment of rutinosyl moiety to the 7-position of pectolinarigenin. Thus, 13 was identified as pectolinarin and also confirmed by comparison these data with those in the literature. This is the first report of the isolation of 12 and 13 from the genus Lantana.

EXPERIMENTAL

Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a HITACHI I-2001 infrared spectrometer. EIMS and FABMS spectra were measured by Finnigan MAT 95 XL spectrometer. NMR spectra were recorded on Varian VXR-300 or Unity Inova 600 MHz spectrometers with TMS as an internal standard. Optical rotations were measured on a Perkin Elmer 241 MC digital polarimeter. UV spectra were recorded on a Shimadzu UV 260 ultraviolet spectrometer.
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Plant Material

The leaves of Lantana camara L. (yellow flower) were collected in the campus of Providence University, Taichung in July 2000. The plant was identified by Mr. Nien-Yung Chiu (Institute of Chinese Pharmaceutical Sciences, China Medical University).

Extraction and Separation

The air-dried leaves (11.9 Kg) of L. camara were extracted with MeOH under reflux. The extract was concentrated in vacuo. The residue (660 g) was suspended in water and consecutively extracted with ethyl acetate and n-butanol. The ethyl acetate fraction (185 g) was chromatographed on a silica gel column using mixtures of CHCl₃-MeOH as eluent to give three fractions. Fraction I was purified by repeated column chromatography on silica gel eluting with n-hexane-ethyl acetate in order of increasing polarity to afford phytosterols (1, 25 mg), betulonic acid (3, 70 mg), betulinic acid (4, 10 mg), oleanolic acid (5, 1510 mg) and ursolic acid (10, 15 mg). Fraction II was further chromatographed on a silica gel column with n-hexane by increasing amounts of acetone to yield lantadene A (6, 20 mg), lantadene B (7, 210 mg), icterogenin (8, 25 mg) and lantanilic acid (9, 5120 mg). Fraction III was rechromatographed on a silica gel column with chloroform and methanol as eluent to give hispidulin (11, 780 mg), pectolinarigenin (12, 5 mg), pectolinarin (13, 25 mg) and β-sitosteryl-3-β-D-glucoside (2, 10 mg).

Pectolinarigenin (12)

Yellow needles (CHCl₃/MeOH), mp: 210-211 °C; IR (KBr) νmax cm⁻¹: 3320 (OH), 1660, 1580; UV λmax nm (MeOH) (log ε): 276 (4.10), 333 (4.20), λmax nm (MeOH + NaOMe) (log ε): 276 (4.22), 296 (4.12), 368 (4.02); λmax nm (MeOH + NaOAc) (log ε): 276 (4.27), 297 (4.10), 368 (4.04); λmax nm (MeOH + AlCl₃) (log ε): 283 (4.06), 300 (4.11), 354 (4.23); ¹H-NMR (600 MHz, CDCl₃/CD₃OD): δ 3.81 (3H, s, 4′-OCH₃), 3.86 (3H, s, 6-OCH₃), 6.47 (1H, s, H-3), 6.48 (1H, s, H-8), 6.94 (2H, d, J = 9.0 Hz, H-3′ and H-5′), 7.77 (2H, d, J = 9.0 Hz, H-2′ and H-6′), 13.08 (1H, br s, 5-OH); ¹³C-NMR (150 MHz, CDCl₃/CD₃OD): δ 60.5 (q, 6-OCH₃), 55.3 (q, 4′-OCH₃), 164.2 (s, C-2), 103.3 (d, C-3), 182.8 (s, C-4), 153.1 (s, C-5), 131.1 (s, C-6), 156.4 (s, C-7), 94.1 (d, C-8), 152.3 (s, C-9), 105.0 (s, C-10), 123.3 (s, C-1’), 127.9 (d, C-2’ and C-6’), 114.3 (d, C-3’ and C-5’), 162.5 (s, C-4’); FABMS m/z (rel. int.%): 315 [M + 1]+ (73), 289 (26), 217 (10), 154 (100), 136 (74).

Pectolinarin (13)

Yellow needles (CHCl₃/MeOH); mp > 300 °C; IR (KBr) νmax cm⁻¹: 3390 (OH), 1660, 1610; UV λmax nm (MeOH) (log ε): 276 (4.10), 333 (4.20), λmax nm (MeOH + NaOMe) (log ε): 276 (4.22), 296 (4.12), 368 (4.02); λmax nm (MeOH + NaOAc) (log ε): 276 (4.27), 297 (4.10), 368 (4.04); λmax nm (MeOH + AlCl₃) (log ε): 283
Acid hydrolysis of 13

A solution of 13 (10 mg) in 5% H₂SO₄ (10 mL) was refluxed for 4 hr. The solid, separated after cooling, was recrystallized from MeOH to give yellow needles (3 mg) of an aglycone (12), mp 210-211 °C. The aqueous layer was concentrated in vacuo. D-glucose and L-rhamnose were identified by TLC on cellulose in pyridine-EtOAc-H₂O (5:5:1:3) Rf 0.4 and 0.6, respectively.

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本研究由黃花馬纓丹 [Lantana camara Linn. (yellow taxa)] 葉部分離得到十三個成分，經光譜分析確定其結構分別為 phytosterols (1), β-sitosterol-3-O-β-D-glucoside (2), betulonic acid (3), betulinic acid (4), oleanolic acid (5), lantadene A (6), lantadene B (7), icterogenin (8), lantanilic acid (9), and ursolic acid (10), hispidulin (11), pectolinarigenin (12)及 pectolinarin (13)。其中 pectolinarigenin (12)及 pectolinarin (13)是馬纓丹屬植物文獻上未曾報導的成分。

關鍵詞：黃花馬纓丹，馬鞭草科，三萜類，黃酮類，黃酮類配醣體。

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