

## Triterpenoid and Phenolic Compounds from Two Chilean Celastraceae

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Z. Naturforsch. **54c**, 144–145 (1999);  
received September 21/October 27, 1998

*Maytenus chubutensis* (Speg.) Lourt., O'Don. et Sleum,  
*Maytenus disticha* (Hook. f.) Urban, Celastraceae,  
Isolation, Structure Elucidation

Three triterpenoid quinonemethides, one triterpene ( $\beta$ -amyrin) and three phenolic compounds were isolated from the roots of *Maytenus chubutensis* (Speg.) Lourt., O'Don. et Sleum. and *Maytenus disticha* (Hook. f.) (Celastraceae). The triterpenoid quinonemethides were identified as tingenone, celastrol and pristimerin. The triterpenoid was identified as  $\beta$ -amyrin and phenolic compounds were identified as catechin, galocatechin and (-)epicatechin.

### Introduction

Plants of the family Celastraceae are well known for their medicinal use (Brüning and Wagner, 1978; Zhu *et al.*, 1998). Extracts derived from some plants of this family have been shown to possess an array of biological activities, including cytostatic, antitumor, antileukaemic and abortifacient activity (Muñoz *et al.*, 1996). These results along with the recent isolation of biologically active compounds from its members have raised current interest in plants belonging to the family Celastraceae (Gamlathe *et al.*, 1986; Corsino *et al.*, 1998).

*M. chubutensis* and *M. disticha* are two Andean species; earlier papers described the isolation of various secondary sesquiterpene metabolites from their aerial parts (Muñoz *et al.*, 1996), and some of these compounds exhibit insecticidal and/or antifeedant activity.

As part of a research program on secondary metabolites from species of the Celastraceae used in Chilean folk medicine, we report a chemical study on the roots of these species. Previous chemical studies on roots of *M. magellanica* (Lam.) Hook. f., other Chilean Celastraceae, resulted in isolation of several known quinonemethides along with a novel dimer formed by pristimerin units (González *et al.*, 1994).

### Materials and Methods

#### General

Melting points are uncorrected, solvents used for NMR: CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub>. The measurements of the NMR spectra were carried out on a Bruker WP-200 SY spectrometer [<sup>1</sup>H NMR (200 MHz), <sup>13</sup>C NMR (50 MHz)] and on a Bruker AMX-300 [<sup>1</sup>H NMR (300 MHz), <sup>13</sup>C NMR (75 MHz). EI-MS (70 eV); VG-Micromass LTD-ZAB-2F.

#### Plant material

*M. chubutensis* and *M. disticha* roots were collected in December 1994 in Talca, Chile, and identified by Prof. J. San Martín, Department of Botany, Talca University. A voucher sample is on deposit in the herbarium of the Chemistry Department, University of Chile, Santiago.

#### Extraction and isolation

The bark of the roots of *M. chubutensis* (320 g) and *M. disticha* (612 g) were separately extracted with 900 ml hexane-Et<sub>2</sub>O 1:1 (v/v) at room temperature for two weeks, respectively. Filtration and evaporation of the solvent with a rotavapor *in vacuo* gave reddish-brown extracts (14 g and 25 g, respectively) which were chromatographed on Sephadex LH-20 (Pharmacia Biotech AB) using a mixture of hexane-CHCl<sub>3</sub>-MeOH 5:5:10 (v/v/v) as solvent and 100 ml fractions were collected in both cases. The extract of *M. chubutensis* was subjected to repeated chromatography on silica gel 60 (MN Kieselgel 60, 50–200  $\mu$ m) with a hexane-EtOAc gradient (0–100% EtOAc) resulting in 14 fractions of increasing polarity. Only fractions 5, 10 and 12 were studied since they showed the pres-

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ence of the major products, whereas the remaining fractions were complex mixtures.

The  $\text{CH}_2\text{Cl}_2$  insoluble part of fraction 10 was dissolved in  $\text{CH}_2\text{Cl}_2$ -MeOH (1:1), chromatographed on 70 g silica gel 60 ( $\text{CH}_2\text{Cl}_2$ -EtOAc, 5:3 v/v) and applied to preparative TLC (EtOAc-acetone, 6:3) yielding **2** (102 mg). Fraction 12 was successively applied to column chromatography (CC) using silica gel (Merck 60G) with a hexane-EtOAc gradient (0–100% EtOAc) followed by an EtOAc-MeOH gradient (0–100% MeOH) afforded **3** (105 mg). Further purification of fractions was achieved using a Chromatotron apparatus and preparative TLC to give **4** (91 mg). Fraction 5 was applied to CC on silica gel 60 (70 g). Fractions were eluted with  $\text{CH}_2\text{Cl}_2$ -MeOH gradient (20–80% MeOH) yielding **5** (10.5 mg).

*M. disticha* was subjected to repeated chromatography on silica gel with a hexane-EtOAc gradient (0–100% EtOAc) followed by an EtOAc-MeOH gradient (0–100% MeOH), resulting 22 fractions of increasing polarity. Only fractions 3, 7, and 20 were studied for similar reason as indicated for *M. chubutensis*.

Fraction 7 was chromatographed on Sephadex LH-20 ( $\text{CH}_2\text{Cl}_2$ -MeOH, 1:2) and silica gel 60 (EtOAc-MeOH, 8:2) yielding **6** (91 mg). Fraction 20 was applied to CC on silica gel 60 (EtOAc-MeOH, 1:2 v/v) and applied to preparative TLC ( $\text{CH}_2\text{Cl}_2$ -MeOH, 3:5 v/v) yielding **7** and **8** (20.3 and 53.0 mg, respectively). Fraction 3 was chromatographed on silica gel 60 ( $\text{CH}_2\text{Cl}_2$ -EtOAc 9:1 v/v), but the products obtained were similar to fraction 20.

## Results

Eight compounds were isolated and characterized from *M. disticha*: tingenone **1** (45 mg), celastrol **2** (21 mg), pristimerin **3** (18 mg) (Fig. 1),  $\beta$ -amyrin **4** (50 mg), catechin **5** (60 mg) and from *M. chubutensis*: **3** (15 mg), galocatechin **6** (50 mg) and (-)epicatechin **7** (15 mg).

All compounds were identified by  $^1\text{H}$  NMR. Galocatechin and (-)epicatechin were further elu-

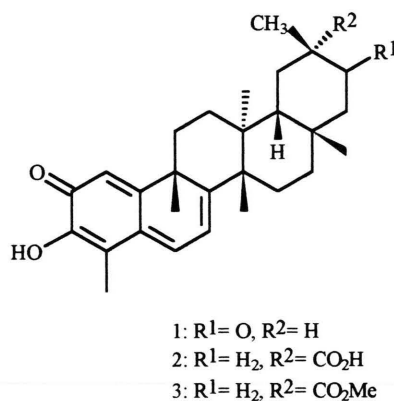


Fig. 1. Chemical structure of quinomethide triterpenoids **1–3**.

cidated by  $^{13}\text{C}$  NMR. In addition, the structure of tingenone was confirmed by EIMS and the identities of **4** and **5** were established by direct comparison with authentic samples by TLC and NMR.

Although none of the compounds isolated in this study were new natural products, this is the first time that their occurrence is reported in roots or leaves of *M. chubutensis* or *M. disticha*.

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