Triterpenoid and Phenolic Compounds from Two Chilean Celastraceae

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

Three triterpenoid quinonemethides, one triterpene (β-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 β-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 posses 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 (Gamlath *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.

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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: $CDCl_3$, DMSO-d_6. The measurements of the NMR spectra were carried out on a Bruker WP-200 SY spectrometer [^{1}H NMR (200 MHz), ^{13}C NMR (50 MHz)] and on a Bruker AMX-300 [^{1}H NMR (300 MHz), ^{13}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_2O 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-$CHCl_3$-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 μm) 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 CH_2Cl_2 insoluble part of fraction 10 was dissolved in CH_2Cl_2-MeOH (1:1), chromatographed on 70 g silica gel 60 (CH_2Cl_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 CH_2Cl_2-MeOH gradient (20–80% MeOH) yielding **5** (10.5 mg).

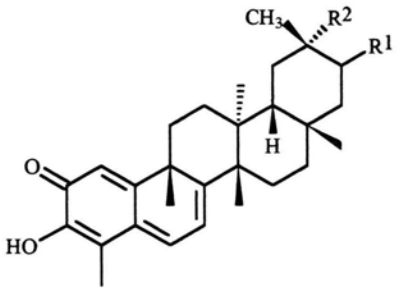
M. disticha was subjected to repeated chromatography on silica gel with a hexane-EtOAc gradient (0–100% EtOAc) followed by an EtOAc-MeOH gradient (0–100% MeOH), resulting 22 fractions of increasing polarity. Only fractions 3, 7, and 20 were studied for similar reason as indicated for *M.chubutensis*.

Fraction 7 was chromatographed on Sephadex LH-20 (CH_2Cl_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 (CH_2Cl_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 (CH_2Cl_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), β-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 ^1H NMR. Galocatechin and (-)epicatechin were further elucidated by ^{13}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.



1: R^1= O, R^2= H
2: R^1= H_2, R^2= CO_2H
3: R^1= H_2, R^2= CO_2Me

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

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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