New Caffeic Acid Esters from *Plazia daphnoides*

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Two new 3,4 dihydroxycinnamic acid esters have been isolated from *Plazia daphnoides*. The structures were elucidated by NMR spectroscopy.

Key words: Plazia daphnoides, Asteraceae, 3,4 Dihydroxycinnamic Acid Esters

Introduction

In the course of continuing studies on plants of the tribe *Mutisieae* (Asteraceae), widely distributed in Chile, with 30 genus and 203 species (Marticorena and Quezada; 1995; Cabrera; 1977) from this tribe several characteristic groups of natural products have been isolated. Some of them in part are typical for the subtribe *Gochnatiinae*, where the *Plazia* genus has been placed (Zdero *et al.*, 1988a). Previously, the oil of *Plazia daphnoides* was destillated and analyzed isolating phenols and volatile fatty acids. Also the aerial parts where examined isolating kolavenol, the flavanoids naringerin, sakuranetin, isokuranetin, acacetin and genkwanin, lupeyl acetate, α- and γ-curcumene, (–)-9-acetoxycapric acid, the 5-methyl coumarins lycoserone and its 1'-epimer, cyclolycoserone and its dehydroderivative (Fester *et al.*, 1958; Zdero *et al.*, 1988b).

In a continuation of our investigation of Chilean Mutisieae (Galvez *et al.*, 1986; Hoeneisen and Becker, 1986; Hoeneisen and Silva, 1986; Maldonado *et al.*, 1988; Hoeneisen *et al.*, 1993, 1997, 1999, 2000) here we report the isolation and structure elucidation of two new compounds: isobutyl-3,4-dihydroxycinnamate (**1**) and 2-methyl-2-butenyl-3,4-dihydroxycinnamate (**2**) from the aerial parts of *Plazia daphnoides*, a species which has not been subjected to a thorough phytochemical analysis.

Materials and Methods

General experimental procedures

^{1}H-NMR were recorder at 400 MHz and ^{13}C-NMR at 100 MHz on Bruker spectrometers, chemical shifts (ppm) are related to $(CH_3)_4Si$ as internal reference.

Plant material

Aerial parts from *P. daphnoides* were collected in Tiliviri (3210 m. s. m.), Prov. Parinacota (I Region, Chile). Voucher specimen (Matthei and Rodriguez 248) can be found at the botanical collection of the herbarium (CONC), Departamento de Botánica, Facultad de Ciencias Naturales y Oceanograficas, Universidad de Concepción, Concepción, Chile.

Isolation and purification of isobutyl-3,4-dihydroxycinnamate (**1**) *and 2-methyl-2-butenyl-3,4-dihydroxycinnamate* (**2**)

Dried plant material (3.0 kg) was crushed and percolated at room temperature with MeOH, which was evaporated under vaccuum, the residue (409 g) was dissolved in H_2O. The solution was partitioned with n-hexane (3 × 500 ml), CH_2Cl_2 (3 × 500 ml) and EtOAc (3 × 500 ml). The CH_2Cl_2, evaporated to dryness, afforded 230,9 g of CH_2Cl_2 extract. This was fractionated by flash chromatography eluting with n-hexane with increasing 10% volume amounts of EtOAc and finally 100%

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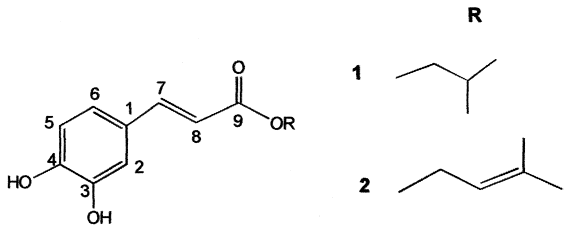

Fig. 1. Caffeic acid ester isolated from *P. daphnoides*.

Table I. ^{1}H and ^{13}C NMR data for compounds isolated from *Plazia daphnoides*. Coupling constants Hz in parenthesis.

	Compound **1**		Compound **2**	
Carbon	δH	δC	δH	δC
1		127.0		
2	7.09 d (2)	115.4	7.08 d (2)	
3		144.1		
4		146.8		
5	6.95 dd (2,6)	114.3	6.93 dd (2,8)	
6	6.87 d (8)	122.5	6.86 d (8)	
7	7.56 d (16)	145.6	7.56 d (16)	145.7
8	6.24 d (16)	114.9	6.23 d (16)	
9		168.8		168.7
1′	3.98 d (7)	71.1	4.70 brd (7)	61.9
2′	2.00 tqq (7,7,7)	27.7	5.40 bst (7)	118.2
3′	0.97 d (7)	19.1	1.76 brs	139.6
4′		19.1	1.72 brs	27.7
5′				18.0

MeOH. The residue from the fraction eluted with 20% EtOAc in CH_2Cl_2 (14 g) was chromatographed over Sephadex LH20 and afforded isobutyl-3,4-dihydroxycinnamate (**1**) and 2-methyl-2-butenyl-3,4-dihydroxycinnamate (**2**) (Fig. 1) by eluation with acetone. They were separated by preparative TLC using $CHCl_3$-MeOH (4:1 v/v).

Results and Discussion

The ^{1}H NMR spectrum of **1** exhibited signals for three aromatic protons in a 2,5,6 substitution pattern, two broad hydroxyl singlets (δ 5.65 and δ 6.05), which together with two protons of a *trans*-doble bond (J = 16 Hz), indicated the presence of a 3,4-dihydroxy-*trans*-cinnamate (caffeate) moiety. Further signal for a deshielding indicated the presence of a small alkyl chain. The carbon spectrum (Table I) confirmed the presence of a dihydroxy cinnamate derivative with resonances attributable to a carbonyl group (δ 168.8), two deshielded oxygen bearing quaternary carbon. The structure of compound **2** was deduced from the NMR data , which are similar to those of **1**, but showing a different signal for the methyl groups at the alkyl chain.

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