

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 distilled and analyzed isolating phenols and volatile fatty acids. Also the aerial parts were 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

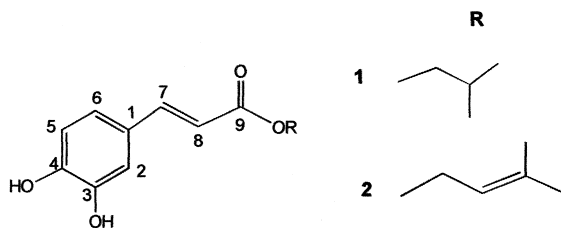
¹H-NMR were recorded at 400 MHz and ¹³C-NMR at 100 MHz on Bruker spectrometers, chemical shifts (ppm) are related to (CH₃)₄Si as internal reference.

Plant material

Aerial parts from *P. daphnoides* were collected in Tiliviri (3210 m.s.m.), Prov. Paríacota (I Region, Chile). Voucher specimen (Matthei and Rodríguez 248) can be found at the botanical collection of the herbarium (CONC), Departamento de Botánica, Facultad de Ciencias Naturales y Oceanográficas, 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 vacuum, the residue (409 g) was dissolved in H₂O. The solution was partitioned with n-hexane (3 × 500 ml), CH₂Cl₂ (3 × 500 ml) and EtOAc (3 × 500 ml). The CH₂Cl₂, evaporated to dryness, afforded 230.9 g of CH₂Cl₂ extract. This was fractionated by flash chromatography eluting with n-hexane with increasing 10% volume amounts of EtOAc and finally 100%

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

Compound 1			Compound 2	
Carbon	δ H	δ C	δ H	δ C
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 tq (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

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

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 elution with acetone. They were separated by preparative TLC using CHCl_3 -MeOH (4:1 v/v).

Results and Discussion

The ^1H 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*-double 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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- Cabrera, A. (1977), Mutisieae-systematic review. In: The Biology and Chemistry of the Compositae (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.). Academic Press, London, pp. 1039–1066.
- Fester G. A., Martinuzzi E. A., Retamar J. and A., Ricciardi A. I. A. (1958), Essential oils from Argentine plants. Bol. Acad. Nac. Cienc. **40**, 189–208.
- Galvez M., Hoeneisen M., Silva M. and Watson W. H. (1986), Germacra-1 (10), 4-dien-*cis*-6,12-olide from *Gochnatia foliolosa* var. *foliolosa*. Bol. Soc. Chil. Quím. **31** (1), 3–5.
- Hoeneisen M. and Becker H. (1986), New Germacranolide flora *Gochnatia foliolosa* var. *foliolosa*. Lloydia **49**, 360–361.
- Hoeneisen M., Hernandez V., Becerra J., Bittner M., Silva M. and Jakupovic J. (1999), Constituents from *Nassauvia pygmaea* and *N. Magellanica*. Phytochemistry **52**, 1667–1669.
- Hoeneisen M., Rojas A., Bittner M., Becerra J., Silva M. and Jakupovic J. (2000), Constituents of *Chuquiraga atacamensis* and *C. ulicina*. Bol. Soc. Chil. Quím. **45**, 49–52.
- Hoeneisen M. and Silva M. (1986), Química y actividad biológica de algunas Compositae chilenas. Rev. Latin Amer. Quím. **17**, 19–24.
- Hoeneisen, M., Silva M., Garrido M. and Jakupovic J. (1997), Constituents from *Nassauvia pygmaea* and *N. Magellanica*. Bol. Soc. Chil. Quím. **42**, 203–205.
- Hoeneisen, M., Silva M., Jakupovic J., Papastergion F. and Peter M. G. (1993), Flavanones of *Lophopappus tarapacanus* and triterpenoids of *Pachylaena atriplicifolia*. Phytochemistry **34**, 1653.
- Hoeneisen M., Silva M., Jakupovic J. and Steglich W. (1997), Isocedrene derivatives and other constituents of *Trixis cacaloides*. Bol. Soc. Chil. Quím. **42**, 307–310.
- Hoeneisen M., Silva M. and Jakupovic J. (1997), Coumarins from *Nassauvia cumingii*. Phytochemistry **46**, 1393–1395.
- Maldonado Z., Hoeneisen M. and Silva M. (1988), New dithiophene flora *Aphyllocladus denticulatus*. Phytochemistry **27**, 2993–2994.
- Marticorena, C. and Quezada, M. (1995), Catalog of the vascular flora of Chile. Gayana Botánica **42**, 5–155.
- Zdero, C., Bohlmann, F. and Niemeyer, H. M. (1988a), 5-methylcoumarin derivatives from *Aphyllocladus denticulatus*. Phytochemistry **27**, 1821.
- Zdero C., Bohlmann F. and Niemayer H. (1988b), Diterpenes and 5-methyl coumarin derivatives from *Gypothamnium pinifolium* and *Plazia daphnoides*. Phytochemistry **27**, 2953–2959.