Pergamon

PII: S0031-9422(97)00828-5

Phytochemistry, Vol. 48, No. 6, pp. 1075–1077, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

A CHROMENE FROM *PIPER ADUNCUM*

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Key Word Index—*Piper aduncum*; Piperaceae; stems; fruits; chromene; flavonoids.

Abstract—A new chromene, methyl 2,2-dimethyl-8-(3-methyl-2-butenyl)-2H-chromene-6-carboxylate, present in a mixture of eupatoriochromene, and mono- and sesquiterpenes from *Piper aduncum* was identified by spectroscopic analysis. In addition, seven known flavonoids and a mixture of sitosterol and stigmasterol were also isolated and identified. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Piper aduncum L. is a small tree (3–8 m), commonly found in Southeast Brazil. It is widely used in folk medicine to treat trachoma, vaginitis and stomach aches [1]. Previous phytochemical investigation of this species has shown the presence of benzoic acid derivatives, chromenes and flavonoids with cytotoxic and antibacterial activities [2–5]. In the present paper, we report the identification of a new chromene (**1**) in addition to eupatoriochromene, monoterpenes and sesquiterpenes (Table 1), 5-hydroxy-7-methxoyflavone (**2**), 2′,6′-dihydroxy-4′-methoxychalcone (**3**), 7-hydroxy-5-methoxydihydroflavone (**4**), 2′-hydroxy-4′,6′-dimethoxydihydrochalcone (**5**), 2′,6′-dihydroxy-4′-methoxydihydrochalcone (**6**), 2′,4-dihydroxy-4′,6′,3-trimethoxydihydrochalcone (**7**), 2′,4-dihydroxy-4′-6′-dimethoxydihydrochalcone (**8**), and a mixture of sitosterol and stigmasterol.

RESULTS AND DISCUSSION

Compound **1** comprising 40% of a mixture was identified by GC-MS analysis (Table 1). The mass spectrum corresponding to the GC signal with R_t 32.89 min, showed $[M]^+ = m/z$ 286. This M_r is in agreement with $C_{18}H_{22}O_3$. The 1D and 2D ^{1}H NMR of this mixture showed two aromatic protons at δ 7.50 and 7.70 with $J_{A,B} = 2.0$ Hz; two olefinic protons in an AB system at δ 5.65 and 6.30 with $J_{A,B} = 10.0$ Hz; a *gem*-dimethyl group attached to an oxygen-bearing carbon at δ 1.40 (6H, *s*); among other signals. These data suggested that **1** was a chromene. Comparison of the ^{1}H NMR and ^{13}C NMR assignments of **1** with published data for 2,2-dimethyl-8-(3-methyl-2-butenyl)-2H-chromene-6-carboxylic acid [4], showed **1** to be a methyl ester (Table 2). A sharp methyl singlet at δ 3.85 in the ^{1}H NMR spectrum and signals at δ 51.61 and at 167.58 in the ^{13}C NMR spectrum, corresponding to a methoxy and an ester carbonyl groups respectively, support this proposal. The other compounds present in the mixture were analysed by GC-MS and the chemical characterization was performed with literature data [6–7] (Table 1).

Table 1. Substances from *P. aduncum* (stems) identified by GC-MS

Compound	R_t (min)	%
β-Pinene	6.04	< 1.00
Myrcene	6.05	< 1.00
α-Phellendrene	6.94	< 1.00
α-Terpinene	7.34	< 1.00
m-Cimene	7.44	< 1.00
1,8-Cineole	7.69	7.86
Bornyl acetate	7.75	< 1.00
Neryl acetate	17.04	< 1.00
Geranyl acetate	17.20	< 1.00
Copaene	17.35	2.05
Caryophyllene	19.88	3.01
Eupatoriochromene	24.22	17.81
1	32.89	40.00

1 = methyl 2,2-dimethyl-8-(3-methyl-2-butenyl)-2H-chromene-6-carboxylate.

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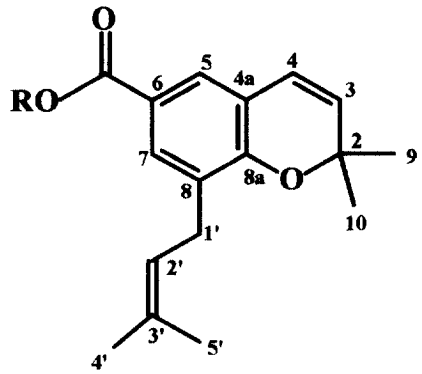
Table 2. Comparison of ^{13}C NMR data (50.2 MHz, $CDCl_3$) of **1** and 2,2-dimethyl-8-(3-methyl-2-butenyl)-2H-chromene-6-carboxylic acid (**2**)

C	1	2
2	77.2	77.2
3	130.7	130.9
4	122.1	122.0
4a	120.4	120.5
5	126.6	125.8
6	121.6	121.8
7	131.7	130.6
8	129.3	129.1
8a	155.4	155.3
9+10	28.3	28.2
1′	28.2	29.6
2′	122.0	121.5
3′	132.5	132.3
4′	25.8	25.6
5′	17.9	17.7
COOR	$R = CH_3$, 167.6	$R = H$, 171.2
$COOCH_3$	51.61	



EXPERIMENTAL

General

UV: MeOH; EIMS 70 eV; ^1H NMR (200 MHz) and ^{13}C NMR (50.2 MHz): $CDCl_3$ using TMS as int. standard.

Separation

CC: Silica gel (Merck); GC: Varian Star 3400 GC, fused silica capillary column (DB-1, 30 m × 0.20 mm), He as carrier gas and temp. programming from 40°–240° (5°/min); GC-MS: HP5890 SII GC coupled to a VG Autospect mass spectrometer at 70 eV, fused silica capillary column (DB-1, 30 m × 0.20 mm), H_2 as carrier gas and temp. programming from 40°–240° (5° min).

Plant material

Stems and fruits of *P. aduncum* were collected near Carmo and fruits of *P. aduncum* were collected near Volta Redonda, Rio de Janeiro State, Brazil. Voucher samples are deposited in the Herbarium of Rio de Janeiro Botanical Garden, Rio de Janeiro, Brazil.

Extraction and isolation

The dried and powdered plant material (stems 1750 g; fruits 150 g) was submitted to successive extraction with hexane, CH_2Cl_2 and MeOH at room temp. The extracts were evapd to dryness under red. pres. The hexane extract of stems (7.76 g) of *P. aduncum* from Carmo, was fractionated by silica gel CC eluted with mixts of hexane–EtOAc and EtOAc–MeOH to give **1** along to eupatoriochromene, and mono- and sesquiterpenes (10 mg). The fraction eluted from this column with a hexane-EtOAc (9:1) was purified over a Sephadex LH-20 column to give **2** (20 mg) and a mixture of sitosterol and stigmasterol (35 mg). The CH_2Cl_2 extract of fruits (7.0 g) collected in Carmo, was chromatographed on a silica gel column using mixts of hexane–EtOAc and EtOAc–MeOH to afford **3** (90.0 mg) and **4** (65.0 mg). The hexane extract of fruits (8.3 g) collected in Volta Redonda, was subjected to CC over silica gel, eluting with mixts of hexane-EtOAc and EtOAc–MeOH to give **5** (90.0 mg) and **6** (75.0 mg). The CH_2Cl_2 extract of fruits (5.0 g) collected in Volta Redonda, was fractionated by silica gel CC using mixts of hexane–EtOAc and EtOAc–MeOH to afford **7** (8.0 mg). The fraction eluted with hexane–EtOAc (3:2) was chromatographed on a XAD-2 column using MeOH as eluent to give **8** (10.0 mg).

Methyl 2,2-dimethyl-8-(3-methyl-2-butenyl)-2H-chromene-6-carboxylate. UV λ_{max}^{MeOH} nm (ε): 346 (0.93), 282 (3.98), 254 (4.0), 239 (4.0); ^1H NMR (200 MHz, $CDCl_3$): δ 1.40 (6H, *s*, CH_3-2), 1.90 (6H, *s*, CH_3-4′, 5′), 3.40 (2H, *d*, $J = 7.0$ Hz, H-1′), 3.85 (3H, *s*, O-CH_3), 5.30 (1H, *t*, $J = 7.0$ Hz, H-2′), 5.65 (1H, *d*, $J = 10.0$ Hz, H-3), 6.30 (1H, *d*, $J = 10.0$ Hz, H-4), 7.50 (1H, *d*, $J = 2.0$ Hz, H-5), 7.70 (1H, *d*, $J = 2.0$ Hz, H-7); ^{13}C NMR: Table 2; GC-MS *m/z* (rel. int.): 286 $[M]^+$ (15), 271 $[M-15]^+$ (100), 255 (5), 227 (2), 197 (7), 128 (10), 115 (9), 91 (7), 77 (7).

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