PERGAMON

Phytochemistry 60 (2002) 799–801

PHYTOCHEMISTRY

www.elsevier.com/locate/phytochem

Two chromones from *Peperomia vulcanica*

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Received 20 January 2002; received in revised form 23 May 2002

Abstract

Two chromones: 5-hydroxy-2-(14′-(*E*)-nonadecenyl) chromone (**1**) and 5-hydroxy-2-[12′-(3″,4″-methylenedioxyphenyl)dodecanyl] chromone (**2**), together with six known compounds have been isolated from *Peperomia vulcanica* Baker & C. H. Wright (Piperaceae). Their structures were determined by spectroscopic analysis including 2D NMR techniques.

Keywords: *Peperomia vulcanica*; Piperaceae; Chromone; Peperovulcanone A and B

1. Introduction

Some *Peperomia* species have been used as folk medicine e.g. *Peperomia vulcanica* Baker & C. H. Wright, a herb which grows on Mount Cameroon and parts of the North West province of Cameroon is being used against sterility and *Peperomia japonica* Makino is used for the treatment of malignant tumors (Chen et al., 1989). Compared with the genus *Piper* of this family, few phytochemical studies of *Peperomia* have been reported (Toshiyuki et al., 1998). However, some compounds like prenylated phenols with antiparasitic activity were reported from *Peperomia galioides* H. B. K. (Mahiou et al., 1995; 1996). In this paper, we describe the isolation and structural determination of two new chromones from *Peperomia vulcanica*.

2. Results and discussion

A sample of *Peperomia vulcanica* was air-dried and powdered (2 kg) and macerated at room temperature in hexane for 6 days, filtration and concentration afforded a dark greenish extract (43 g). Vacuum liquid chromatography of this extract on silica gel followed by repeated column chromatography afforded the new compounds peperovulcanone A (**1**) and peperovulcanone B (**2**) and the previously described 2,3-bis (3,4 -dimethoxybenzyl)-4,5-dihydro-2(3H)-furanone (Estévez-Braun et al., 1996); sesamin (Andrew et al., 1976); yangambin (Andrew et al., 1976); kusunokinol (Brown and Daugan, 1989); campestan-3,6-dione (Fernández et al., 1983) and ergost-6,22-dien-3,5,8-triol (Zhen-Fu et al., 1997) which were identified by comparison of their physical and spectroscopic data with those in the literature.

Compound **1** was obtained as a yellow oil. The EIMS showed a molecular peak at m/z 426 compatible with molecular formula $C_{28}H_{42}O_3$. Its IR spectrum indicated the presence of a hydroxyl group at 3300 cm^{-1} and a carbonyl at 1650 cm^{-1}. In the ^1H NMR spectrum (Table 1) four aromatic protons signals were observed at 7.48 (1H, *t*, J = 8.3 Hz), 6.85 (1H, *dd*, *J* = 8.3, 0.9 Hz), 6.76 (1H, *dd*, *J* = 8.3, 0.9 Hz) and 6.09 (1H, *s*) and a chelated hydroxyl proton at δ 12.56, suggesting a chromone skeleton with hydroxy group at C-5. Additional signals present at δ 5.34 and 5.30 were attributed to a double bond in a long aliphatic chain signal at δ 1.26. The ^{13}C NMR spectrum (Table 1) showed signals of a carbonyl group at δ 183.6 and oxygenated sp^2 carbons at δ 171.3, 160.8 and 156.8. In the COSY spectrum

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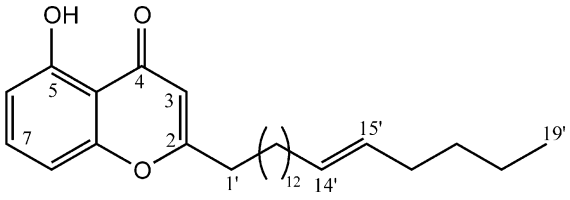
0031-9422/02/$ - see front matter
PII: S0031-9422(02)00191-7

Table 1
NMR data of compound **1** ($CDCl_3$, *J* values in Hz are given in parentheses)

Position	δ_C	δ_H	HMBC H to C
2	171.27		
3	108.33	6.09, *s*	2, 4, 1′
4	183.57		
4a	156.80		
5	160.79	12.56 (OH)	
6	106.79	6.85 (*dd*, 8.3, 0.9)	4a, 5, 7, 8
7	134.98	7.48 (*t*, 8.3)	5, 6, 8, 8a
8	111.08	6.76 (*dd*, 8.3, 0.9)	6, 7, 8a
8a	110.57		
1′	34.30	2.60 (*t*, 7.7)	2, 3, 2′
2′	26.88	1.72 (*quintet*, 7.4)	2, 1′, 3′
3′–11′	29.70–28.94	1.35–1.26, *m*	
12′	31.93	1.38, *m*	11′, 13′, 14′
13′	27.19	2.01 (*t*, 5.6)	11′, 12′, 14′
14′	129.83	5.34 (*dt*, 11.2, 5.6)	12′, 13′, 15′, 16′
15′	129.76	5.30 (*dt*, 11.2, 5.6)	13′, 14′, 16′, 17′
16′	27.15	2.01 (*t*, 5.6)	14′, 15′, 17′, 18′
17′	31.73	1.38, *m*	15′, 16′, 18′, 19′
18′	22.66	1.35–1.26, *m*	16′, 17′, 19′
19′	14.07	0.88 (*t*, 7.9)	17′, 18′

^1H–^1H correlations were observed between proton at 7.48 (H-7) and protons at 6.85 (H-6) and 6.76 (H-8). This led us to suggest structure **1** for the compound. Peaks *m*/*z* 329 and 43 due to allylic cleavage of C14′–C15′ confirmed the nature of the side chain and position of the double bond. Long-range coupling ^1H–^{13}C couplings deduced from the HMBC spectrum (Table 1) were in agreement with the structure.

Compound **2** was obtained as white crystals in hexane, mp 85–86 °C. The EIMS gave a molecular ion peak at *m*/*z* 450 compatible with molecular formula $C_{28}H_{34}O_5$. The ^1H NMR spectrum (Table 2) showed a superimposable chromone moiety as observed in compound **1** with additional proton signals [6.72 (1H, *d*, *J* = 7.9 Hz), 6.67 (1H, *d*, *J* = 1.6 Hz), 6.61 (1H, *dd*, *J* = 7.9, 1.6 Hz)] which were attributed to additional aromatic ring moiety. A methylenedioxy group was also observed at δ 5.90 as well as a saturated aliphatic side chain between δ 2.60–1.25. The ^{13}C NMR spectrum (Table 2) showed in addition to chromone moiety, signals at 147.4, 145.4, 136.8, 108.8, 108.1, 121.0, 100.5, 34.3 and 35.6 attributed with the aid of HMQC spectrum to C-3″, C-4″, C-1″, C-2″, C-5″, C-6″, OCH_2O, C-1′ and C-12′ respectively. The COSY spectrum showed the following H–H cross peaks between H-12′ and H-6″ and between H-2″ and H-6″ with H-5″ which enabled us to assign structure **2** (a chromone moiety linked to a piperonyl moiety by 12 methylene carbons) to peperovulcanone B. Analysis of the HMBC spectrum showed pertinent H–C correlations such as H-1′ to C-2 and C-2′ and H-12′ to C-1″ and C-11′ which further confirmed structure **2**.



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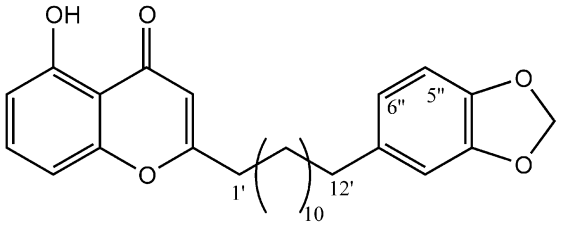

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3. Experimental

3.1. General method

Melting points were recorded with a Kofler hot stage 277938 and are uncorrected. ^1H NMR (400.13 MHz) and ^{13}C NMR (100.6 MHz) were registered in $CDCl_3$

Table 2
NMR data of compound **2** ($CDCl_3$, *J* values in Hz are given in parentheses)

Position	δ_C	δ_H	HMBC (H to C)
2	171.28		
3	108.00	6.10, *s*	2, 4, 4a, 1′
4	183.61		
4a	156.82		
5	160.82	12.56 (OH)	
6	106.79	6.85 (*dd*, 8.3, 0.9)	4a, 5, 7, 8
7	135.02	7.49 (*t*, 8.3)	5, 6, 8, 8a
8	111.08	6.76 (*dd*, 8.3, 0.9)	6, 7, 8a
8a	108.38		
1′	34.32	2.60 (*t*, 7.8)	2, 3, 2′
2′	26.69	1.71, *m*	2, 1′, 3′
3′	28.93	1.38–1.25, *m*	1′, 2′, 4′
4′–10′	29.12–29.69	″	
11′	31.70	1.56, *m*	10′, 12′, 1″
12′	35.66	2.53 (*t*, 7.5)	11′, 1″, 2″, 6″
1″	136.77		
2″	108.83	6.67 (*d*, 1.6)	1″, 3″, 4″
3″	147.42		
4″	145.41		
5″	108.10	6.72 (*d*, 7.9	1″, 3″, 4″, 6″
6″	121.00	6.61 (*dd*, 7.9, 1.6)	1″, 2″, 4″, 5″
OCH_2O	100.50	5.90, *s*	

with a Bruker DPX 400 spectrometer. Chemical shifts are reported in parts per million (ppm) and coupling constants in hertz (Hz). IR spectra were registered with JASCO FTIR-410 spectrometer. UV spectra were recorded with Shimadzu UV-3101 PC. Mass spectra were obtained by EI with a Jeol JMS 700 spectrometer at 70 eV. TLC plates were visualised with UV light (254 and 366 nm) and sprayed with 50% H_2SO_4 and other reagents followed by heating in an oven. Silica gel 60 (70–230 mesh) was used for CC while Silica gel F_{254} was used for TLC.

3.2. Plant material

The whole plant material of *Peperomia vulcanica* Baker & C. H. Wright (Piperaceae) was collected in Awing, North West Province of Cameroon in October 1998. Authentication was done by Paul Mezili, a retired botanist of the Cameroon National Herbarium, Yaounde. A voucher specimens (UD 422) has been deposited at the herbarium of the Botany Department, University of Dschang.

3.3. Extraction and isolation

Air-dried whole plant (2 kg) of *Peperomia vulcanica* was macerated in hexane at room temperature for 6 days. Filtration and concentration on a rotavapor led to a dark greenish extract (43 g). Vacuum liquid chromatography on silica gel eluted with gradients of EtOAc in hexane led to six main fraction (500 ml fractions collected and combined on the basis of TLC profiles) of increasing polarity. F1 obtained with 2% EtOAc was chromatographed on silica gel eluted with a gradiant of EtOAc in hexane. The first ten subfractions were combined and rechromatographed on silica gel column (toluene/hexane [7:3]) and then purified by MPLC using the Bæckström Separo AB column (hexane) and silica gel column (hexane/EtOAc [98:2]) afforded **1** (100 mg). The following fractions were purified by gel permeation on Sephadex LH-20 (hexane/CH_2Cl_2 [7:3]) afforded**2** (3 mg). F3 obtained with 10% EtOAc was stripped off chlorophyll by gel permeation through Sephadex LH-20 (CH_2Cl_2/ MeOH [8:2]) and subsequently purified on a silica gel column eluted with a gradient of EtOAc in hexane leading to sesamin (124 mg), campestan-3,6-dione (16mg) and ergost-6,22-dien3,5,8-triol (15 mg). F5 obtained with 20% EtOAc was chromatographed twice on silica gel column (CH_2Cl_2/acetone [97:3]) affording 2,3-bis (3,4-dimethoxybenzyl)-4,5-dihydro-2(3*H*)-furanone (200 mg), yangambin (55 mg) and kusunokinol (15 mg).

3.4. Spectroscopy

3.4.1. Peperovulcanone A (*1*)

Compound **1** was obtained as a yellow oil. UV λ_{max}^{MeOH} nm (log ϵ): 326.5 (4.3), 234 (4.9). IR υ_{max}^{KBr} cm^{-1}: 3300, 2920, 2851, 1650, 1591, 1465, 1407, 1257, 1231. EIMS (70 eV), *m*/*z* (rel.int.): 426 [M^+] (4), 398 (14), 373 (35), 329 (12), 315 (10), 245 (10), 189 (100), 176 (35), 43 (11); anal. C 78.80%, H 9.93%, calc. for $C_{28}H_{42}O_3$, C 78.82% H 9.92%. ^1H and ^{13} C NMR data [$CDCl_3$ (Table 1)].

3.4.2. Peperovulcanone B (*2*)

Compound **2** was obtained as white crystal (hexane), mp 85–86 °C. IR υ_{max}^{KBr} cm^{-1}: 3410, 2920, 2850, 1653, 1621, 1470, 1408, 1233, 1190, 752. EIMS *m*/*z* (rel. Int.): 450 [M^+] (20), 422 (70), 189 (100), 176 (25); anal. C 74.66%, H 7.60%, calc. for $C_{28}H_{34}O_5$, C 74.64% H 7.61%. ^1H and ^{13}C NMR data [$CDCl_3$ (Table 2)].

Acknowledgements

Financial support from the International Science Program, Uppsala University is gratefully acknowledged.

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