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TWO 6,7-DIOXYGENATED COUMARINS FROM *PTEROCAULON VIRGATUM*

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Key Word Index—*Pterocaulon virgatum*; Compositae; 6,7-dioxygenated coumarins; virgatenol; virgatul.

Abstract—From the petrol and chloroform extracts of the aerial parts of *Pterocaulon virgatum*, two new coumarins, virgatenol and virgatul, were isolated, as well as the four known coumarins, 7-(3-methyl-2-butenyloxy)-6-methoxycoumarin, 7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin, ayapin (6,7-methylenedioxy coumarin) and scopoletin (7-hydroxy-6-methoxycoumarin). Their structures were elucidated on the basis of spectroscopic methods. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Pterocaulon virgatum is widely distributed in north eastern Argentina, southern Brazil and Paraguay. Aerial parts of this plant are used in Argentine traditional medicine as a digestive, an emenagogue, an insecticide and as an agent against snake bites [1–4].

In previous papers, we have reported the isolation of four 5,6,7-trioxygenated coumarins [5, 6], five flavonoids [7], caffeic acid, chlorogenic acid, isochlorogenic acid and 3,4-dicaffeoylquinic acid [8–9] from the aerial parts of *P. virgatum*. In a continuing investigation, we have now isolated and identified six coumarins from the same source. Two of them are new compounds, named virgatenol (**1**) and virgatul (**2**), and four were the known coumarins, 7-(3-methyl-2-butenyloxy)-6-methoxycoumarin, 7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin, ayapin and scopoletin.

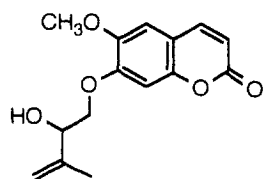
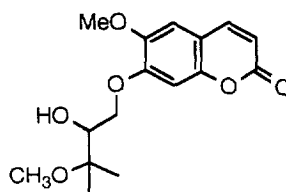
RESULTS AND DISCUSSION

The aqueous methanol extract of aerial parts was subjected to successive extraction with petrol, chloroform, ethyl ether and ethyl acetate. Combined fractionation procedures of the petrol and chloroform extracts, based on the use of preparative TLC and column chromatography with Sephadex and silica gel, and various solvent systems, succeeded in affording

coumarins **1**, **2**, 7-(3-methyl-2-butenyloxy)-6-methoxycoumarin and ayapin from the petrol extract, and 7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin and scopoletin from the chloroform extract. Amongst these, virgatenol (**1**) and virgatul (**2**) represent novel natural coumarins, while 7-(3-methyl-2-butenyloxy)-6-methoxycoumarin, ayapin, and scopoletin are being reported for the first time in *Pterocaulon*. The known coumarin, 7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin, is also present in another two species of *Pterocaulon*, namely *P. lanatum* and *P. balansae* [10]. Complete physical and spectroscopic data of the latter coumarin and ayapin, not previously reported in the literature, are also given in this paper.

Compounds **1** and **2** exhibited diagnostic UV spectra with absorption maxima at 295 and 345 nm [11]. The IR spectra showed the presence of a lactone carbonyl, typical of coumarins, at 1724 cm⁻¹ for **1** and at 1720 cm⁻¹ for **2**. The ¹H NMR spectra of both compounds (Table 1) showed a typical pair of doublets at δ 6.30 and 7.62 ($J = 9.4$ Hz) (**1**) and at δ 6.27 and 7.61 ($J = 9.4$ Hz) (**2**) for H-3 and H-4, respectively. The relatively high field position of H-4 in **1** and **2** suggested the lack of an oxygen substituent at C-5 [12]. Two uncoupled aromatic protons at δ 6.87 (2H) for **1** and two singlet signals at δ 6.87 and 6.85 (1H, each) for **2**, characteristic of H-5 and H-8, were a clear indication of a 6,7-dioxygenated pattern in the aromatic nucleus. In addition, both coumarins showed a methoxyl singlet signal at δ 3.90 (3H) for **1** and δ 3.88 (3H) for **2**. Compounds **1** and **2** differed

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**1** Virgatenol**2** Virgatol

only in the nature of the ether side-chain. Compound **1** exhibited two pairs of double doublets at δ 4.0 ($J = 9.6, 8.2$ Hz) and 4.15 ($J = 9.6, 2.8$ Hz) corresponding with the AB-part of an ABX system in a O—CH₂—CH—O— moiety, and a doublet of doublet at δ 4.56 ($J = 8.2, 2.8$ Hz) showing the X-portion of the same system. In addition, the ¹H NMR spectrum exhibited two broad singlet signals at δ 5.04 and 5.17 (1H, each), typical of terminal vinylic protons, and a broadened singlet signal at δ 1.84 (3H) characteristic of a methyl group, suggesting the presence of a CH₂=C(CH₃) fragment. Compound **2** showed a multiplet signal at δ 4.01 (2 H) and a doublet of doublets at δ 4.26 ($J = 9.2, 2.0$ Hz) corresponding with the AB-part of an ABX-system in a O—CH₂—CH—O— fragment. A singlet signal at δ 3.27 (3H, OMe) and a singlet signal at δ 1.26 (6H, Me₂) suggested the presence of a (CH₃)₂C—OCH₃ fragment. The EI mass spectra of **1** and **2** exhibited, in addition to the [M]⁺ m/z 276 and 308, respectively, an intense fragment at m/z 192 [M—R]⁺, undergoing facile loss of 15 mu, to give the ion at m/z 177 [M—R—CH₃]⁺. This type of fragmentation reveals that the aromatic methoxyl group must be linked to C-6 [11].

The ¹³C NMR spectra of **1** and **2** were assigned from off-resonance decoupled spectra and by DEPT pulse sequence for **1** (Table 2). The spectroscopic data of virgatenol (**1**) are in agreement with the structure 7-(2-hydroxy-3-methyl-3-butenyloxy)-6-methoxycoumarin [13]. It should be noted that this compound was first isolated from *P. virgatum* [14]. The structure of the new natural coumarin, virgatol (**2**), was determined to be 7-(2-hydroxy-3-methoxy-3-methylbutenyloxy)-6-methoxycoumarin.

The ¹H NMR spectra of 7-(3-methyl-2-butenyloxy)-6-methoxycoumarin and 7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin exhibited (Table 1) typical H-3 and H-4 doublets, and a singlet signal at δ 3.87 (3H) for the former and δ 3.89 (3H) for the latter compound. In addition, two uncoupled aromatic protons at δ 6.82 (2H) for the former and at δ 6.84 (1H) and 6.85 (1H) for the latter compound, which are characteristic of H-5 and H-8 in 6,7-disubstituted coumarins, were attributed. 7-(3-Methyl-2-butenyloxy)-6-methoxycoumarin showed characteristic signals of a 3-methyl-2-butenyloxy side-chain. The IR, mp, EI mass and ¹³C NMR spectra (Table 2) were in accordance with the proposed structure and identical with

Table 1. ¹H NMR spectral data of the five coumarins isolated (270 MHz; CDCl₃)

H	1 (virgatenol)	2 (virgatol)	7-(3-methyl-2-butenyloxy)-6-methoxycoumarin	7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin	ayapin
3	6.30 <i>d</i> ($J = 9.4$ Hz)	6.27 <i>d</i> ($J = 9.4$ Hz)	6.25 <i>d</i> ($J = 9.6$ Hz)	6.29 <i>d</i> ($J = 9.5$ Hz)	6.28 <i>d</i> ($J = 9.5$ Hz)
4	7.62 <i>d</i> ($J = 9.4$ Hz)	7.61 <i>d</i> ($J = 9.4$ Hz)	7.59 <i>d</i> ($J = 9.6$ Hz)	7.61 <i>d</i> ($J = 9.5$ Hz)	7.58 <i>d</i> ($J = 9.5$ Hz)
5	6.87 <i>s</i>	6.87 <i>s</i>	6.82 <i>s</i>	6.85 <i>s</i>	6.82 <i>s</i>
8	6.87 <i>s</i>	6.85 <i>s</i>	6.82 <i>s</i>	6.84 <i>s</i>	6.82 <i>s</i>
6,7-OCH ₂ O	—	—	—	—	6.10 <i>s</i>
6-OMe	3.90 <i>s</i>	3.88 <i>s</i>	3.87 <i>s</i>	3.89 <i>s</i>	—
1'	4.00 <i>dd</i> ($J = 9.6, 8.2$ Hz)	4.01 <i>m</i>	4.65 <i>d</i> ($J = 6.9$ Hz)	4.13 <i>dd</i> ($J = 9.7, 6.1$ Hz)	—
	4.15 <i>dd</i> ($J = 9.6, 2.8$ Hz)	4.26 <i>dd</i> ($J = 9.2, 2.0$ Hz)		4.29 <i>dd</i> ($J = 9.7, 2.5$ Hz)	—
2'	4.56 <i>dd</i> ($J = 8.2, 2.8$ Hz)	4.01 <i>m</i>	5.46 <i>t</i> ($J = 6.9$ Hz)	3.80 <i>m</i>	—
3'	—	—	—	—	—
4'	5.04 <i>s</i>	—	1.74 <i>s</i>	1.33 <i>s</i>	—
	5.17 <i>s</i>	—	—	—	—
3'-Me	1.84 <i>s</i>	1.26 <i>s</i>	1.76 <i>s</i>	1.29 <i>s</i>	—
3'-OMe	—	3.27 <i>s</i>	—	—	—
2'-OH	2.75 <i>br s</i>	2.58 <i>br s</i>	—	2.88 <i>br s</i>	—
3'-OH	—	—	—	3.24 <i>br s</i>	—

Table 2. ^{13}C NMR (68 MHz) spectral data† of the five coumarins isolated (CDCl_3)

C	1‡	2	7-(3-Methyl-2-butenyloxy)-6-methoxycoumarin	7-(2,3-Dihydroxy-3-methylbutyloxy)-6-methoxycoumarin	Ayapin
2	161.3 (s)	161.40 (s)	161.50 (s)	161.2 (s)	161.2 (s)
3	114.0 (d)	113.55 (d)	113.28 (d)	114.0 (d)	113.4 (d)
4	142.9 (d)	143.3 (d)	142.9 (d)	143.2 (d)	143.4 (d)
4a	112.1 (s)	111.7 (s)	112.1 (s)	112.1 (s)	112.7 (s)
5	108.6 (d)	108.4 (d)	108.6 (d)	108.2 (d)	105.0 (d)
6	146.8 (s)	146.7 (s)	146.8 (s)	146.5 (s)	143.4 (s)
7	151.9* (s)	152.2* (s)	152.0 (s)	151.6* (s)	151.3 (s)
8	102.0 (d)	101.5 (d)	101.1 (d)	101.5 (d)	98.4 (d)
8a	149.8* (s)	149.8* (s)	149.8 (s)	149.8* (s)	144.9 (s)
6,7- OCH_2O					102.3 (t)
6-OMe	56.4 (q)	56.3 (q)	56.3 (q)	56.3 (q)	—
1'	73.0 (t)	70.5 (t)	66.2 (t)	71.4 (t)	—
2'	73.3 (d)	74.9 (d)	118.5 (d)	74.9 (d)	—
3'	143.2 (s)	76.0 (s)	139.0 (s)	71.9 (s)	—
4'	113.2 (t)	20.4 (q)	25.8 (q)	25.6 (q)	—
3'-Me	18.9 (q)	21.2 (q)	18.4 (q)	26.6 (q)	—
3'-OMe	—	49.3 (q)	—	—	—

* Assignments may be interchanged.

† Multiplicity from off-resonance decoupled spectra in parentheses.

‡ Assignments were based on 2D ^1H - ^{13}C (one bond) correlation experiments (Cl_3CD , 270 MHz).

the previously reported physical and spectroscopic data [15]. 7-(2,3-Dihydroxy-3-methylbutoxy)-6-methoxycoumarin showed two doublets of doublets at δ 4.13 (1H, $J = 9.7, 6.1$ Hz) and δ 4.29 (1H, $J = 9.7, 2.5$ Hz), which coupled with a broad multiplet at δ 3.80 (1H), indicative of the presence of a $\text{CH}_2\text{—CH—O}$ moiety. The presence of two aliphatic hydroxyl groups was clearly demonstrated from the broad signals at δ 3.24 and 2.88 (1H each). The loss of 15 mu in the EI mass spectrum, giving the ion at m/z 177 $[\text{M—R—CH}_3]^+$, confirmed the C-6 methoxyl substituent [11]. The ^{13}C NMR spectrum (Table 2) fully supported the structure as 7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin. These results were in accordance with previously reported data [16], but, here a more complete characterization is reported.

The ^1H NMR spectra of ayapin (6,7-methylenedioxy coumarin) showed diagnostic H-3 and H-4 olefinic doublets at δ 6.28 and 7.58 (Table 1). The 6,7-dioxygenation pattern of the aromatic ring was confirmed by a singlet signal at δ 6.82 (2H), corresponding to H-5 and H-8. The presence of a two-proton signal at δ 6.10 as a singlet is characteristic of a methylenedioxyphenyl group. The EI mass and ^{13}C NMR spectra (Table 2) supported the structure of ayapin (6,7-methylenedioxy coumarin). These results were in accordance with previously reported data [17], but, as far as we know, this is the first report on the complete spectral data of this compound.

The widely distributed scopoletin was identified by co-chromatography with an authentic sample and by comparison of its spectroscopic data with those previously reported [18].

EXPERIMENTAL

General

Mps: uncorr. UV spectra: MeOH. IR: KBr pellet. EIMS were obtained by direct probe insertion at 70 eV. ^1H and ^{13}C NMR were recorded at 270 and 68 MHz, respectively, in CDCl_3 using TMS as int. standard. The following types of silica gel were used: Merck 7734.1000 for CC and 60-PF254 for TLC. Sephadex LH-20 (Sigma 82 H 0368) was also used for CC.

Plant material. Aerial parts of *P. virgatum* (L.) DC were collected from the Experimental Station INTA, Concepción del Uruguay, Entre Ríos, Argentina, during November 1989. A voucher specimen is deposited at the Botanical Museum "Juan A. Dominguez" in Buenos Aires, Argentina. Classification as number SD 041 was performed by Dr B. Sorarú.

Extraction and isolation. Air-dried and powdered aerial parts (950 g) were extracted at room temp. with 25% aq. MeOH. The MeOH was removed under red. pres. and the aq. layer partitioned between petrol. CHCl_3 , Et_2O and EtOAc , successively. The concd petrol extract (1 g) was subjected to CC on silica gel and eluted successively with a petrol– EtOAc mixts of increasing polarity. Frs (15 ml) were collected and monitored by silica gel TLC in system A: CHCl_3 –MeOH (19:1), B: CHCl_3 – Et_2O (7:3), and C: toluene– CHCl_3 – Me_2CO (10:10:0.8). Frs 20–24, containing 7-(3-methyl-2-butenyloxy)-6-methoxycoumarin and ayapin, were separated by prep. TLC in system C to give 20 mg of the former and 25 mg of ayapin. Frs

48–54 were subjected to CC on silica gel eluted with CHCl_3 –MeOH (9:1) to yield 25 mg of virgatenol (1) and 10 mg of virgatol (2).

The CHCl_3 extract (2.4 g) was subjected to CC on Sephadex LH20 and eluted with benzene, containing increasing amounts of CHCl_3 . Frs 21–25 were combined and, after recrystallization from MeOH, yielded 35 mg of 7-(2,3-dihydroxy-3-methylbutoxy)-6-methoxycoumarin. Frs 26–29 were chromatographed on silica gel using CHCl_3 –MeOH (9:1) to give scopolin.

Virgatenol (7-(2-Hydroxy-3-methyl-3-butenyloxy)-6-methoxycoumarin) (1). R_f in system A: 0.81 and B: 0.23. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 345, 292, 250 sh, 230. IR ν_{max} cm^{-1} : 3400, 3030, 2930, 2870, 1724, 1630, 1580, 1470, 1390, 1330, 1265, 1130, 830, 758. EIMS m/z (rel. int.): 276 $[\text{M}]^+$ ($\text{C}_{15}\text{H}_{16}\text{O}_5$, 33), 234 $[\text{M}-\text{C}_3\text{H}_5]^+$ (5), 192 $[\text{M}-\text{R}+\text{H}]^+$ (100), 177 $[\text{192}-\text{CH}_3]^+$ (17), 164 $[\text{192}-\text{CO}]^+$ (15), 149 $[\text{164}-\text{CH}_3]^+$ (14); ^1H NMR: see Table 1; ^{13}C NMR: see Table 2.

Virgatol (7-(2-Hydroxy-3-methyl-3-methoxybutoxy)-6-methoxycoumarin) (2). White powder, mp 60–62°. R_f in system A: 0.77 and B: 0.17. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 345, 292, 250 sh, 230. IR ν_{max} cm^{-1} : 3400, 3030, 2930, 2850, 1720, 1625, 1580, 1520, 1460, 1400, 1380, 1300, 1280, 1190, 1100, 1010, 928, 860, 820, 755. EIMS m/z (rel. int.): 308 $[\text{M}]^+$ ($\text{C}_{16}\text{H}_{20}\text{O}_6$, 9), 192 $[\text{M}-\text{R}]^+$ (36), 177 $[\text{192}-\text{CH}_3]^+$ (8), 164 $[\text{192}-\text{CO}]^+$ (5), 149 $[\text{164}-\text{CH}_3]^+$ (9), 73 $[\text{C}(\text{Me})_2\text{OMe}]^+$ (100), 69 (10), 55 (10). ^1H NMR: Table 1. ^{13}C NMR: Table 2.

7-(3-Methyl-2-butenyloxy)-6-methoxycoumarin. Colourless needles, mp 82–84° (lit. 80–82°). R_f in system A: 0.93, B: 0.71 and C: 0.40. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 345, 292, 250 sh, 230. IR ν_{max} cm^{-1} : 3052, 2972, 1715, 1630, 1555, 1505, 1270, 1140 cm^{-1} . EIMS m/z (rel. int.): 260 $[\text{M}]^+$ ($\text{C}_{15}\text{H}_{16}\text{O}_4$, 2), 192 $[\text{M}-\text{R}+\text{H}]^+$ (100), 177 $[\text{192}-\text{CH}_3]^+$ (30), 164 $[\text{192}-\text{CO}]^+$ (24), 149 $[\text{164}-\text{CH}_3]^+$ (18). ^1H NMR: Table 1. ^{13}C NMR: Table 2.

7-(2,3-Dihydroxy-3-methylbutoxy)-6-methoxycoumarin. Colourless crystals, mp 143–145° (lit. oil). R_f in system A: 0.48 and B: 0.05. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 345, 292, 250 sh, 230. IR ν_{max} cm^{-1} : 3400, 3080, 2960, 1710, 1630, 1580, 1525, 1470, 1435, 1380, 1330, 1280, 1210, 1160, 1100, 1020, 930, 860, 830, 760. EIMS m/z (rel. int.): 294 $[\text{M}]^+$ ($\text{C}_{15}\text{H}_{18}\text{O}_6$, 30), 192 $[\text{M}-\text{R}]^+$ (100), 177 $[\text{192}-\text{CH}_3]^+$ (21), 164 $[\text{192}-\text{CO}]^+$ (14), 149 $[\text{164}-\text{CH}_3]^+$ (8), 59 $[\text{C}(\text{Me})_2\text{OH}]^+$ (43). ^1H NMR: Table 1. ^{13}C NMR: Table 2.

Ayapin (6,7-methylenedioxycoumarin). Colourless needles, mp 221–223° (lit. 231–232°). R_f in system A: 0.92, B: 0.67 and C: 0.45. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 345, 292, 250 sh, 230. IR ν_{max} cm^{-1} : 3050, 2920, 1720, 1630, 1580, 1515, 1470, 1380, 1270, 1220, 1100, 1040, 950, 880, 800, 760. EIMS m/z (rel. int.): 190 $[\text{M}]^+$ ($\text{C}_{10}\text{H}_6\text{O}_4$, 100), 162 $[\text{M}-\text{CO}]^+$ (73), 161 (53), 104 (8), 81 (13), 79 (13), 78 (9), 69 (10), 58 (10), 53 (15), 51 (19), 50

(23), 44 (19), 43 (33). ^1H NMR: Table 1. ^{13}C NMR: Table 2.

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