

5-METHYL COUMARINS AND CHROMONES FROM *TRIPTILION* SPECIES

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Key Word Index—*Triptilion benaventei*, *T. spinosum*; Compositae; 5-methyl coumarins; 5-methyl chromones.

Abstract—The aerial parts of two *Triptilion* species afforded in addition to known compounds eight new 5-methyl coumarins and a related chromone. The structures were elucidated by high field NMR techniques. The chemotaxonomic relevance of these findings are discussed briefly.

INTRODUCTION

The genus *Triptilion* (Compositae, tribe Mutisieae) is concentrated in Central Chile and placed in a group which is characterized by few phyllaries and florets and a similar exine structure [1]. As nothing was known on the chemistry of this genus we have studied two species, *T. benaventei* Remy and *T. spinosum* R. et P. var. *spinosum*. The results are presented in this paper.

RESULTS AND DISCUSSION

The aerial parts of *Triptilion benaventei* afforded the 5-methyl coumarin derivatives **1**, **2a/b**, **4** and **5a/b**. The structure of compound **1** followed from the ¹H NMR spectrum (Table 1) which was in part close to those of several 5-methyl coumarins isolated from *Ethulia cyanoides* [2–6] where, however, different side chains at C-5' are present. The nature of the side chain of **1** clearly followed from the corresponding ¹H NMR signals. The configuration of the Δ⁶ bond was determined by a NOE between H-6' and H-8'. We have named this compound triptiliocoumarin.

The spectra of the epimers **2a/b**, which could not be separated, followed also from the ¹H NMR spectral data (Table 1) and from that of the anhydro derivative **3**. The latter was obtained as the only product on treatment of the epimers **2a/b** with acetic anhydride. The configuration of the Δ⁶ bond again was determined by NOE. The stereochemistry at C-5' of the epimers **2a/b** followed from comparison of the chemical shifts of H-2' with those of related compounds from an *Ethulia* species [1]. Furthermore, if a 5α'-hydroxy is present a *W*-coupling with H-4β' can be observed while in the case of a 5β'-hydroxy derivative [1] a *W*-coupling between the 3'-methyl group and H-4α' is present.

As already followed from the molecular formula (C₂₅H₃₀O₅) the coumarin **4** had one oxygen more than **2a/b**. As one olefinic methyl signal was replaced by a sharp singlet, and furthermore a sharp singlet at δ 3.13 was present, an 6', 7'-epoxide of **2b** was very likely. This was further supported by a *W*-coupling between H-4' and the hydroxy proton which required an axial orientation of the hydroxy group which is hydrogen bonded with the

epoxide oxygen leading to a very sharp doublet for the hydroxyl proton. The relative configuration at C-3' and C-5' again was deduced from the corresponding chemical shifts of the neighbouring protons.

The structures of the epimers **5a** and **5b** followed from the ¹H NMR spectra (Table 1) which were in part similar to that of cyclobrachycoumarin from a *Mutisia* species [7] where a geranyl moiety is linked with the coumarin in the same way. The relative configuration at C-2' and C-3' in the case of **5b** was determined by a NOE between H-1' and H-15' (7%). Accordingly, **5a** is isotriptiliocoumarin and **5b** 2'-epiisotriptiliocoumarin.

The extract of the aerial parts of *Triptilion spinosum* gave umbelliferone, the chromones **6a** (nassauvia chromone) [8], **6b** [8] and **6c** as well as the 5-methyl coumarins **2c** and **7**.

The ¹H NMR spectrum of compound **2c** was in part very close to that of **1**. However, the aromatic protons led to a pair of doublets at δ 7.09 and 7.05 indicating an additional oxygen function at C-8. As already followed from the mass spectrum this could only be a hydroxy group, accordingly in the NMR a broadened singlet at δ 4.96 was observed.

The structure of **6c** could be established by comparing the ¹H NMR spectrum (Table 1) with that of **6b** [8]. The replacement of the carbomethoxy by an aldehyde group followed from the absence of a methoxy signal while a singlet at δ 9.41 required an aldehyde proton its chemical shift indicated the E-configuration of the Δ¹⁰ bond. As the signals of H-1'–H-5' and H-15' were nearly identical with those of **6a** and **6b**, where the configuration at C-3' and C-5' was established, identical stereochemistry also for **6c** was likely. The absolute configuration of all compounds could not be determined.

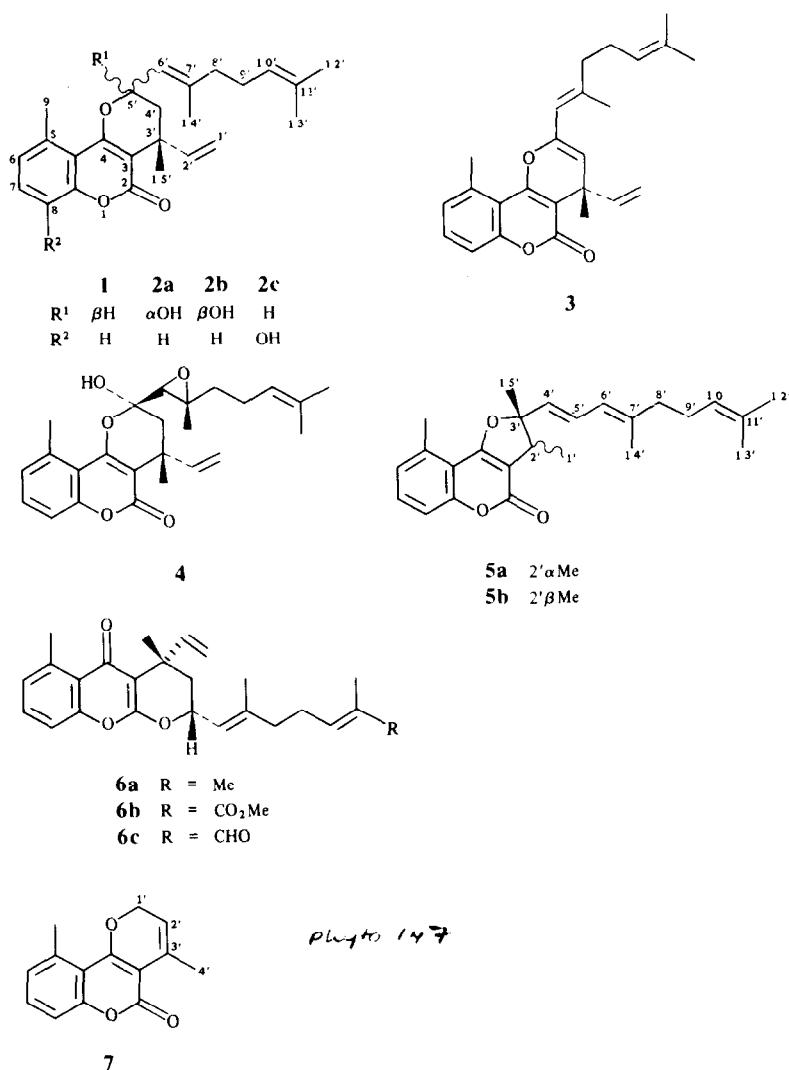
The molecular formula of **7** (C₁₄H₁₂O₃), which we have named triptispinocoumarin, already indicated that a degraded compound was present. The ¹H NMR spectrum (see Experimental) showed that in this case the 4-hydroxy-5-methyl coumarin was condensed with a C₄-unit.

The chemistry of the genus *Triptilion* again shows that the rare 5-methyl coumarins and chromones are characteristic of groups in the tribe Mutisieae. As the chromones **6a** and **6b** has been isolated from *Nassauvia* [8] the

Table 1. ¹H NMR spectral data of compounds **1**, **2a–2c**, **3**, **4**, **5a**, **5b** and **6c** (400 MHz, CDCl₃; δ -values)

H	1	2a	2b	2c	3	4	5a	5b	6c
6	6.99 <i>br d</i>	7.01 <i>br d</i>	7.00 <i>br d</i>	7.09 <i>br d</i>	7.02 <i>br d</i>	7.02 <i>br d</i>	7.04 <i>br d</i>	7.02 <i>br d</i>	7.05 <i>br d</i>
7	7.30 <i>t</i>	7.35 <i>t</i>	7.33 <i>t</i>	7.05 <i>d</i>	7.33 <i>t</i>	7.34 <i>t</i>	7.38 <i>t</i>	7.37 <i>t</i>	7.38 <i>t</i>
8	7.12 <i>br d</i>	7.16 <i>br d</i>	7.15 <i>br d</i>	—	7.14 <i>br d</i>	7.15 <i>br d</i>	7.21 <i>br d</i>	7.19 <i>br d</i>	7.16 <i>br d</i>
9	2.64 <i>br s</i>	2.72 <i>br s</i>	2.75 <i>br s</i>	2.77 <i>s</i>	2.71 <i>br s</i>	2.73 <i>br s</i>	2.71 <i>br s</i>	2.69 <i>br s</i>	2.83 <i>br s</i>
1'	{5.14 <i>d</i> (t)}	{5.24 <i>d</i> (t)}	{5.08 <i>d</i> (t)}	{5.13 <i>dd</i> (t)}	{5.10 <i>dd</i> (t)}	{5.17 <i>dd</i> (t)}	1.19 <i>d</i>	1.33 <i>d</i>	{5.13 <i>d</i> }
	{5.11 <i>d</i> (c)}	{5.27 <i>d</i> (c)}	{5.07 <i>d</i> (c)}	{5.09 <i>dd</i> (c)}	{5.21 <i>dd</i> (c)}	{5.11 <i>d</i> (c)}	3.21 <i>q</i>	3.37 <i>q</i>	{5.09 <i>d</i> }
2'	6.17 <i>dd</i>	6.23 <i>dd</i>	6.32 <i>dd</i>	6.16 <i>dd</i>	6.49 <i>dd</i>	6.31 <i>dd</i>	5.70 <i>d</i>	5.75 <i>d</i>	6.16 <i>dd</i>
	{1.95 <i>dd</i> }	{2.42 <i>d</i> }	—	{1.95 <i>dd</i> }	4.79 <i>s</i>	{2.11 <i>d</i> }	6.58 <i>dd</i>	6.49 <i>dd</i>	{1.96 <i>dd</i> }
4'	{1.75 <i>dd</i> }	{2.05 <i>d</i> }	—	{1.64 <i>dd</i> }	—	{2.04 <i>dd</i> }	5.91 <i>br d</i>	5.83 <i>br d</i>	{1.65 <i>dd</i> }
5'	4.93 <i>ddd</i>	—	—	5.09 <i>ddd</i>	—	—	5.91 <i>br d</i>	—	5.09 <i>ddd</i>
6'	5.39 <i>br d</i>	5.51 <i>br s</i>	5.61 <i>br s</i>	5.34 <i>br d</i>	5.67 <i>br s</i>	3.13 <i>s</i>	—	—	5.41 <i>br d</i>
8'	{2.13 <i>m</i> }	{2.14 <i>m</i> }	—	{2.10 <i>m</i> }	{2.17 <i>br s</i> }	{1.80 <i>m</i> }	{2.10 <i>m</i> }	{2.07 <i>m</i> }	2.54 <i>br q</i>
9'	—	—	—	—	—	{1.62 <i>m</i> }	—	—	2.29 <i>br t</i>
10'	5.10 <i>br t</i>	5.10 <i>br t</i>	5.08 <i>br t</i>	5.09 <i>br t</i>	5.11 <i>br t</i>	2.17 <i>br q</i>	5.10 <i>br t</i>	5.08 <i>br t</i>	6.48 <i>br t</i>
12'	1.70 <i>br s</i>	1.68 <i>br s</i>	1.67 <i>br s</i>	1.70 <i>br s</i>	1.70 <i>br s</i>	5.09 <i>br t</i>	1.68 <i>br s</i>	1.67 <i>br s</i>	9.41 <i>s</i>
13'	1.63 <i>br s</i>	1.62 <i>br s</i>	—	1.57 <i>br s</i>	1.62 <i>br s</i>	1.70 <i>br s</i>	1.60 <i>br s</i>	1.59 <i>br s</i>	1.77 <i>br s</i>
14'	1.76 <i>d</i>	1.89 <i>br s</i>	1.90 <i>br s</i>	1.77 <i>d</i>	1.90 <i>d</i>	1.46 <i>s</i>	1.78 <i>br s</i>	1.74 <i>br s</i>	1.82 <i>d</i>
15'	1.60 <i>s</i>	1.57 <i>s</i>	1.77 <i>s</i>	1.62 <i>s</i>	1.64 <i>s</i>	1.62 <i>s</i>	1.59 <i>s</i>	1.59 <i>s</i>	1.61 <i>s</i>

$J[\text{Hz}]$: 6, 7 = 7, 8 = 8; 6', 14' = 1; compounds **1**, **2a–2c**: 1c', 2' = 10.5; 1t', 2' = 17; 9', 10' = 7; compounds **1** and **2c**: 4₁', 5' = 12; 4₂', 5' = 2; 5', 6' = 8; compounds **2a**, **b** and **4**: 4₁', 4₂' = 14.5; compound **4**: 4₂', OH = 1.5; compounds **5a**, **b**: 1', 2' = 9', 10' = 7; 4', 5' = 15; 5', 6' = 11; compound **6c**: 4₁', 4₂' = 14; 4₂', 5' = 12; 4₂', 5' = 2; 5', 6' = 8; 8', 9' = 9', 10' = 7.



placement of *Triptilion* together with the latter in a closely related group [1] would be supported by the chemistry while that of *Moscharia* and *Polyachyrus*, both also placed in this group [1], differs completely, the former having isocedrenes [9] and the latter highly oxygenated eudesmanes [10]. Further investigations, both of the morphology and the chemistry, are therefore desirable.

EXPERIMENTAL

Air-dried plant material of *T. benaventei* (137 g, collected in January 1986, Parque Nacional, Nahuelbuta, Chile, voucher P. Pacheco 1844) was extracted and worked-up as reported previously [11]. The CC fractions obtained with Et₂O-petrol (1:1), were further sepd by TLC (silica gel, Et₂O-petrol (1:1) and by HPLC (RP 8, MeOH-H₂O (17:3), ca 100 bar). Finally 3 mg **1** (*R_f* 13.1 min), 9 mg **2a/b** (*R_f* 14.6 min and TLC Et₂O-petrol (1:3), three developments, *R_f* 0.66), 2 mg **4** (*R_f* 11.9 min), 5 mg **5a** (*R_f* 14.6 min and TLC Et₂O-petrol (1:3), three developments, *R_f* 0.70) and 2 mg **5b** (*R_f* 14.6 min and TLC Et₂O-petrol (1:3), three developments, *R_f* 0.80) were obtained.

The extract of the aerial parts of *T. spinosum* (135 g, collected in January 1987, Parque Hualpen, Chile, voucher Z. Rozas 2172) gave by CC three fractions [1:Et₂O-petrol (1:3); 2:Et₂O-petrol (3:1) and 3:Et₂O and Et₂O-MeOH (9:1)]. Repeated TLC of fraction 1 [Et₂O-petrol (1:6), several developments] gave 7 mg **6a** and 2 mg **7** (*R_f* 0.45). TLC of fraction 2 [Et₂O-petrol (1:3)] gave 10 mg **6b**, 8 mg **6c** (*R_f* 0.38) and 3 mg **2c** (*R_f* 0.35). TLC of fraction 3 afforded 10 mg umbelliferone. Known compounds were identified by comparing the 400 MHz ¹H NMR spectra with those of authentic materials.

Triptiliocoumarin (1). Colourless gum; IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 1705, 1602 (coumarin); MS *m/z* (rel. int.): 378.220 [M]⁺ (12) (calc. for C₂₅H₃₀O₃: 378.219), 228 [RDA]⁺ (69), 135 [C₈H₇O₂]⁺ (18), 69 [C₅H₉]⁺ (100); [α]_D²⁴ - 22 (CHCl₃; c 0.16).

5'-Hydroxytriptiliocoumarin (2a/b). Colourless gum, which could not be sepd by TLC or HPLC. IR $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 3460 (OH), 1710, 1610, 1600 (coumarin). Heating with Ac₂O/DMAP in CHCl₃ at 70° for 3 hr afforded **3**, colourless gum; MS *m/z* (rel. int.): 376.204 [M]⁺ (22) (calc. for C₂₅H₂₈O₃: 376.204), 361 [M - Me]⁺ (100), 349 [M - CH=CH₂]⁺ (21), 307 [M - C₅H₉]⁺ (40), 173 (63), 69 (41).

8-Hydroxytriptiliocoumarin (2c). Colourless gum; $\nu_{\max}^{\text{CHCl}_3}$ cm⁻¹: 3600 (OH), 1710 (coumarin); MS *m/z* (rel. int.): 394.214

$[M]^+$ (4) (calc. for $C_{25}H_{30}O_4$: 394.214), 325 $[M-C_5H_9]^+$ (8), 244 $[M-C_{11}H_{18}]^+$ (100), 69 $[C_5H_9]^+$ (36); $[\alpha]_D^{24} + 8$ ($CHCl_3$; c 0.18).

5 α '-Hydroxy-6',7'-epoxytriptiliocoumarin (4). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3520 (OH), 1710, 1610, 1600 (coumarin); MS m/z (rel. int.): 410.210 $[M]^+$ (3.5) (calc. for $C_{25}H_{30}O_5$: 410.210), 229 $[M-C_{11}H_{17}O_2]^+$ (66), 135 (86), 95 (54), 69 (100).

Isotriptiliocoumarin (5a). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1710, 1630, 1600 (coumarin); MS m/z (rel. int.): 378.219 $[M]^+$ (16) (calc. for $C_{25}H_{30}O_3$: 378.219), 363 $[M-Me]^+$ (3), 309 $[M-C_5H_9]^+$ (20), 229 (22), 175 (21), 69 (100).

2'-Epiisotriptiliocoumarin (5b). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1710, 1620, 1600 (coumarin); MS m/z (rel. int.): 378.220 $[M]^+$ (38) (calc. for $C_{25}H_{30}O_3$: 378.219), 363 (6), 309 (34), 229 (42), 175 (38), 69 (100).

12'-Oxo-nassauvia chromone (6c). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1710 (CHO), 1650 (chromone); MS m/z (rel. int.): 228 $[M-C_{11}H_{18}]^+$ (100), 213 $[228-Me]^+$ (14), 69 (60); $[\alpha]_D^{24} - 1.5$ ($CHCl_3$; c 0.79).

Triptispinocoumarin (7). Colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1710, 1600 (coumarin); MS m/z (rel. int.): 228.079 $[M]^+$ (90) (calc. for $C_{14}H_{12}O_3$: 228.079), 213 $[M-Me]^+$ (30), 189 (48), 135 (56), 69 (100); 1H NMR ($CDCl_3$): δ 7.01 (*br d*, H-6), 7.35 (*t*, H-7), 7.14 (*br d*, H-8), 2.65 (*br s*, H-9), 4.83 (*dq*, H-1'), 5.41 (*tg*, H-2'), 2.23 (*br q*, H-4'); (J [Hz]: 6, 7 = 7, 8 = 8; 1', 2' = 4; 1', 4' = 1.5; 2', 4' = 1).

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