

## 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  $^1\text{H}$  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  $^1\text{H}$  NMR signals. The configuration of the  $\Delta^{6'}$  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  $^1\text{H}$  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  $\Delta^{6'}$  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  $5\alpha'$ -hydroxy is present a *W*-coupling with H-4 $\beta'$  can be observed while in the case of a  $5\beta'$ -hydroxy derivative [1] a *W*-coupling between the 3'-methyl group and H-4 $\alpha'$  is present.

As already followed from the molecular formula ( $\text{C}_{25}\text{H}_{30}\text{O}_5$ ) 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  $\delta$  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  $^1\text{H}$  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** was 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  $^1\text{H}$  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  $\delta$  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  $\delta$  4.96 was observed.

The structure of **6c** could be established by comparing the  $^1\text{H}$  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  $\delta$  9.41 required an aldehyde proton its chemical shift indicated the E-configuration of the  $\Delta^{10'}$  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.

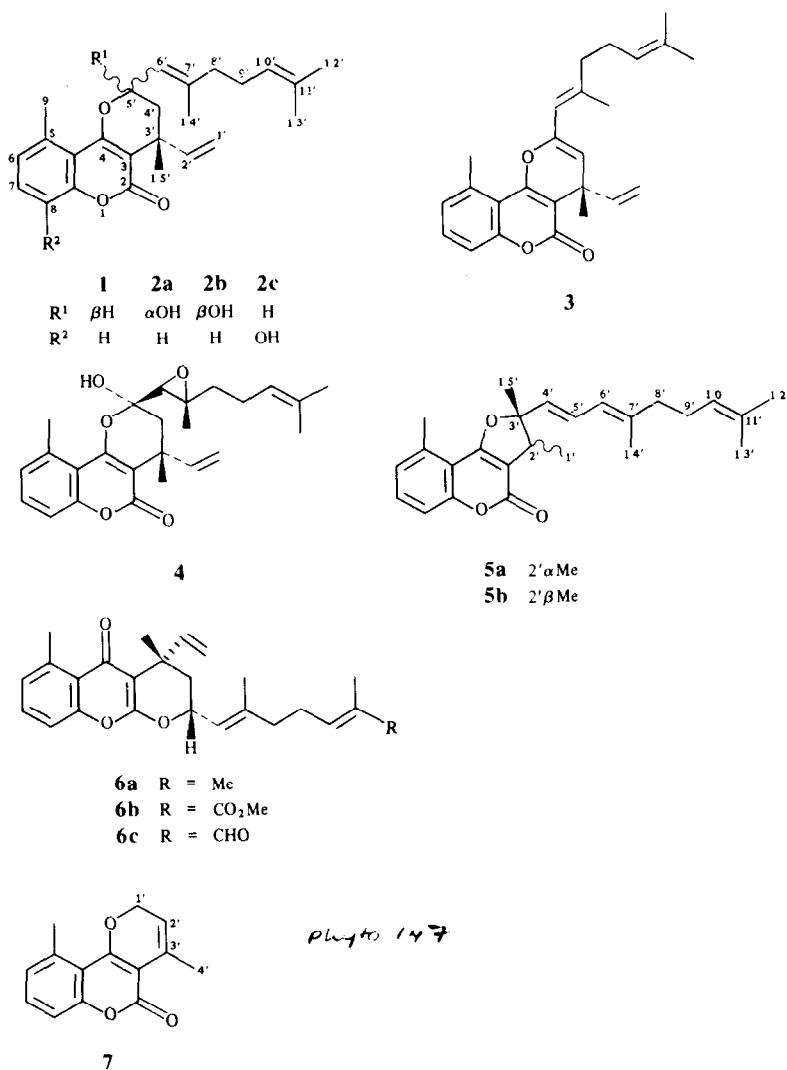
The molecular formula of **7** ( $\text{C}_{14}\text{H}_{12}\text{O}_3$ ), which we have named triptispinocoumarin, already indicated that a degraded compound was present. The  $^1\text{H}$  NMR spectrum (see Experimental) showed that in this case the 4-hydroxy-5-methyl coumarin was condensed with a  $\text{C}_4$ -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.  $^1\text{H}$  NMR spectral data of compounds **1**, **2a**–**2c**, **3**, **4**, **5a**, **5b** and **6c** (400 MHz,  $\text{CDCl}_3$ ;  $\delta$ -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>	7.02 <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> ( <i>t</i> )	5.24 <i>d</i> ( <i>t</i> )	5.08 <i>d</i> ( <i>t</i> )	5.13 <i>dd</i> ( <i>t</i> )	5.10 <i>dd</i> ( <i>t</i> )	5.17 <i>dd</i> ( <i>t</i> )	5.11 <i>d</i>	1.33 <i>d</i>	5.13 <i>d</i>
1'	5.11 <i>d</i> ( <i>c</i> )	5.27 <i>d</i> ( <i>c</i> )	5.07 <i>d</i> ( <i>c</i> )	5.09 <i>dd</i> ( <i>c</i> )	5.21 <i>dd</i> ( <i>c</i> )	5.11 <i>d</i> ( <i>c</i> )	5.09 <i>d</i>	5.09 <i>d</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>	3.21 <i>q</i>	3.37 <i>q</i>	6.16 <i>dd</i>
3'	1.95 <i>dd</i>	2.42 <i>d</i>	—	1.95 <i>dd</i>	—	2.11 <i>d</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>	5.70 <i>d</i>	5.75 <i>d</i>	1.65 <i>dd</i>
5'	4.93 <i>ddd</i>	—	—	5.09 <i>ddd</i>	—	—	6.58 <i>dd</i>	6.49 <i>dd</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>	5.91 <i>br d</i>	5.83 <i>br d</i>	5.41 <i>br d</i>
8'	—	2.13 <i>m</i>	—	2.10 <i>m</i>	2.17 <i>br s</i>	—	—	—	2.54 <i>br q</i>
9'	—	2.14 <i>m</i>	—	—	—	—	—	—	2.07 <i>m</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>	5.09 <i>br t</i>	5.10 <i>br t</i>	5.08 <i>br t</i>	2.29 <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>	1.70 <i>br s</i>	1.68 <i>br s</i>	1.67 <i>br s</i>	6.48 <i>br t</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>	1.63 <i>br s</i>	1.60 <i>br s</i>	1.59 <i>br s</i>	9.41 <i>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>	1.77 <i>br s</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* [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**; 4', 5' = 12; 4<sub>2</sub>', 5' = 2; 5', 6' = 8; compounds **2a**, **b** and **4**; 4<sub>1</sub>', 4<sub>2</sub>' = 14.5; compound **4**; 4<sub>2</sub>', OH = 1.5; compounds **5a**/**b**: 1, 2' = 9, 10' = 7; 4', 5' = 15; 5, 6' = 11; compound **6c**: 4<sub>1</sub>', 4<sub>2</sub>' = 14; 4, 5' = 12; 4<sub>2</sub>', 5' = 2; 5, 6' = 8; 8, 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  $Et_2O$ -petrol (1:1), were further sepd by TLC (silica gel,  $Et_2O$ -petrol (1:1) and by HPLC (RP 8,  $MeOH$ - $H_2O$  (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  $Et_2O$ -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  $Et_2O$ -petrol (1:3), three developments,  $R_f$  0.70) and 2 mg **5b** ( $R_f$  14.6 min and TLC  $Et_2O$ -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:  $Et_2O$ -petrol (1:3); 2:  $Et_2O$ -petrol (3:1) and 3:  $Et_2O$  and  $Et_2O$ - $MeOH$  (9:1)]. Repeated TLC of fraction 1 [ $Et_2O$ -petrol (1:6, several developments) gave 7 mg **6a** and 2 mg **7** ( $R_f$  0.45). TLC of fraction 2 [ $Et_2O$ -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  $\nu_{max}^{CHCl_3}$  cm<sup>-1</sup>: 1705, 1602 (coumarin); MS  $m/z$  (rel. int.): 378.220 [ $M$ ]<sup>+</sup> (12) (calc. for  $C_{25}H_{30}O_3$ : 378.219), 228 [RDA]<sup>+</sup> (69), 135 [ $C_8H_7O_2$ ]<sup>+</sup> (18), 69 [ $C_5H_9$ ]<sup>+</sup> (100);  $[\alpha]^{24}_D$  -22 ( $CHCl_3$ ; *c* 0.16).

**5'-Hydroxytriptiliocoumarin (2a/b).** Colourless gum, which could not be sepd by TLC or HPLC. IR  $\nu_{max}^{CHCl_3}$  cm<sup>-1</sup> = 3460 (OH), 1710, 1610, 1600 (coumarin). Heating with  $Ac_2O$ /DMAP in  $CHCl_3$  at 70° for 3 hr afforded 3, colourless gum; MS  $m/z$  (rel. int.): 376.204 [ $M$ ]<sup>+</sup> (22) (calc. for  $C_{25}H_{28}O_3$ : 376.204), 361 [ $M - Me$ ]<sup>+</sup> (100), 349 [ $M - CH=CH_2$ ]<sup>+</sup> (21), 307 [ $M - C_5H_9$ ]<sup>+</sup> (40), 173 (63), 69 (41).

**8-Hydroxytriptiliocoumarin (2c).** Colourless gum;  $\nu_{max}^{CHCl_3}$  cm<sup>-1</sup>: 3600 (OH), 1710 (coumarin); MS  $m/z$  (rel. int.): 394.214

$[\text{M}]^+$  (4) (calc. for  $\text{C}_{25}\text{H}_{30}\text{O}_4$ : 394.214), 325  $[\text{M} - \text{C}_5\text{H}_9]^+$  (8), 244  $[\text{M} - \text{C}_{11}\text{H}_{18}]^+$  (100), 69  $[\text{C}_5\text{H}_9]^+$  (36);  $[\alpha]_D^{24} + 8$  ( $\text{CHCl}_3$ ;  $c$  0.18).

*5 $\alpha$ '-Hydroxy-6',7'-epoxytriptiliocoumarin (4).* Colourless gum; IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$ : 3520 (OH), 1710, 1610, 1600 (coumarin); MS  $m/z$  (rel. int.): 410.210  $[\text{M}]^+$  (3.5) (calc. for  $\text{C}_{25}\text{H}_{30}\text{O}_5$ : 410.210), 229  $[\text{M} - \text{C}_{11}\text{H}_{17}\text{O}_2]^+$  (66), 135 (86), 95 (54), 69 (100).

*Isotriptiliocoumarin (5a).* Colourless gum; IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$ : 1710, 1630, 1600 (coumarin); MS  $m/z$  (rel. int.): 378.219  $[\text{M}]^+$  (16) (calc. for  $\text{C}_{25}\text{H}_{30}\text{O}_3$ : 378.219), 363  $[\text{M} - \text{Me}]^+$  (3), 309  $[\text{M} - \text{C}_5\text{H}_9]^+$  (20), 229 (22), 175 (21), 69 (100).

*2'-Epiisotriptiliocoumarin (5b).* Colourless gum; IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$ : 1710, 1620, 1600 (coumarin); MS  $m/z$  (rel. int.): 378.220  $[\text{M}]^+$  (38) (calc. for  $\text{C}_{25}\text{H}_{30}\text{O}_3$ : 378.219), 363 (6), 309 (34), 229 (42), 175 (38), 69 (100).

*12'-Oxo-nassauvia chromone (6c).* Colourless gum; IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$ : 1710 (CHO), 1650 (chromone); MS  $m/z$  (rel. int.): 228  $[\text{M} - \text{C}_{11}\text{H}_{18}]^+$  (100), 213  $[\text{228} - \text{Me}]^+$  (14), 69 (60);  $[\alpha]_D^{24} - 1.5$  ( $\text{CHCl}_3$ ;  $c$  0.79).

*Triptispinocoumarin (7).* Colourless gum; IR  $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$ : 1710, 1600 (coumarin); MS  $m/z$  (rel. int.): 228.079  $[\text{M}]^+$  (90) (calc. for  $\text{C}_{14}\text{H}_{12}\text{O}_3$ : 228.079), 213  $[\text{M} - \text{Me}]^+$  (30), 189 (48), 135 (56), 69 (100);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  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 (*tq*, 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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