

COUMARINS FROM *PTEROCAULON BALANSAE* AND *P. LANATUM*

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Abstract—Analysis of the petrol–diethyl ether extracts of *Pterocaulon balansae* and *P. lanatum* aerial parts afforded, besides puberulin, scopoletin–[2',3'-dihydroxy-3'-methylbutyl-(1')] ether, scopoletin–[2',3'-epoxy-3'-methylbutyl-(1')] ether and 7-(3-methyl-2,3-epoxybutyloxy)-5,6-methylenedioxycoumarin, four new related coumarins. The isolation of these coumarins may constitute a valid index for the chemotaxonomic characterization of genus.

INTRODUCTION

The genus *Pterocaulon* has 25–30 species. *P. balansae* Chodat. and *P. lanatum* O. Kuntze subshrubby plants from the Compositae family occur almost exclusively in the central part of the South America [1]. *P. balansae* species is very easily confused with *P. alopecuroides* (Lam.) DC a synonym of *Conyza alopecuroides* Lam. [1]. Some *Conyza* species afford coumarin compounds [2] as well as *P. sphacelatum* Benth & Hook [3], the only *Pterocaulon* species already studied. The present communication deals with the isolation of eight coumarins from the aerial parts of *P. balansae* and *P. lanatum*.

RESULTS AND DISCUSSION

The petrol–Et₂O extracts from the aerial parts of the plants on chromatography yielded substances **1** to **8**. **1**, **2** and **3** are common to both plants, **1** and **6** were first isolated from *Pteronia glabrata* L.f. and *P. ciliata* Thunb. respectively [4], **3** and **5** from *Conyza obscura* DC [2].

Compound **2**, a new isomer of sabandinol (**9**) [5], was elucidated on the basis of spectral data and confirmed by acidic epoxide cleavage of **1**.

Of the remaining three compounds, those of composition C₁₆H₁₈O₆ and C₁₆H₂₀O₇ have UV spectra essentially superimposable on that of **6**, leading to the conclusion that all three have the same oxygenation pattern. ¹H NMR spectra of both substances show signals for C-4 protons at δ 7.57 and δ 7.63 respectively, suggesting the lack of an oxygenated function at C-5. By running ¹H NMR spectra in both CDCl₃ and C₆D₆ it was possible to locate OMe groups at C-6 and C-8 [7]. These data are in agreement with the structures **4** and **8** respectively, which were proved by epoxidation of **6** followed by acidic cleavage of the epoxide.

The last coumarin with composition C₁₅H₁₄O₅ must have a methylene-dioxy group and dimethylallyloxy group which is evident from ¹H NMR analysis (Table 1) through the peaks at δ 6.08 and δ 4.93 respectively. The only aromatic proton must be located at C-8 since the C-4

Table 1. ¹H NMR data of compounds **2**, **4**, **7** and **8** (60 MHz, CDCl₃ and C₆D₆)

	2* CDCl ₃	4 CDCl ₃	4 C ₆ D ₆	7 CDCl ₃	7 C ₆ D ₆	8 CDCl ₃	8 C ₆ D ₆
H-3	6.26 d	6.40 d	6.05 d	6.25 d	5.98 d	6.45 d	6.10 d
H-4	8.05 d	7.65 d	6.75 d	8.04 d	7.66 d	7.75 d	6.81 d
H-5	—	6.75 s	6.12 s	—	—	6.81 s	6.11 s
H-8	6.63 s	—	—	6.60 s	6.34 s	—	—
H-1'	4.40 dd (6, 11)	4.26 d	4.26 dd	4.93 br. d	4.75 d	4.7 m	4.7 m
	4.63 dd (4, 11)	(6)	(6, 10)	(8)	(8)		
H-2'	3.85 m	3.25 t	3.20 m	5.48 br. t	5.48 m	3.8 m	3.8 m
		(6)		(8)			
Me-3'	1.26 s	1.28 s	1.05 s	1.76 s	1.53 s	1.26 s	1.20 s
	1.33 s	1.37 s	1.11 s	1.80 s	1.62 s	1.30 s	1.30 s
O—CH ₂ —O	6.09 s	—	—	6.08 s	5.17 s	—	—
MeO-6	—	3.94 s	3.66 s	—	—	3.98 s	3.23 s
NeO-8	—	4.09 s	3.54 s	—	—	4.15 s	3.99 s

* Saturated soln in C₆D₆ too dilute for reliable assignments of weak signals; δ scale.

Signals are designated as follows: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; br. broad. Figures in parentheses are coupling constants in Hz. J_{3,4} = 10 Hz.

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