COUMARINS FROM PTEROCAULON BALANSAE AND P. LANATUM

ADERBAL F. MAGALHÃES, EVA G. MAGALHÃES, HERMÓGENES F. LEITÃO FILHO,* ROSA T. S. FRIGHETTO and SIMONE M. G. BARROS

Instituto de Química and *Instituto de Biologia, Universidade Estadual de Campinas (UNICAMP), CP 1170, 13100 Campinas, São Paulo, Brazil

(Received 4 September 1980)

Key Word Index-Pterocaulon balansae; P. lanatum; Compositae; new coumarin derivatives.

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 $C_{16}H_{18}O_6$ and $C_{16}H_{20}O_7$ have UV spectra essentially superimposable on that of $\bf 6$, 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 C_6D_6 it was possible to locate OMe groups at C-6 and C-8 [7]. These data are in agreement with the structures $\bf 4$ and $\bf 8$ respectively, which were proved by epoxidation of $\bf 6$ followed by acidic cleavage of the epoxide.

The last coumarin with composition $C_{15}H_{14}O_5$ 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*	4		7		8	
	CDCl ₃	CDCl ₃	C_6D_6	CDCl ₃	C_6D_6	CDCl ₃	C_6D_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 (6)	3.20 m	5.48 br. t (8)	5.48 m	3.8 m	3.8 m
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 C_6D_6 too dilute for reliable assignments of weak signals; δ scale.

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

proton resonates at $\delta 8.04$ [6]. These data suggest two possible structures (7 and 10) from which we choose 7 because of the pronounced diamagnetic shift of the methylenedioxy protons (0.91 ppm) when the ¹H NMR spectrum is recorded in CDCl₃ and C₆D₆ (Table 1) [4].

EXPERIMENTAL

General methods. UV were run in EtOH; IR in KBr pellets: ¹H NMR spectra at 60 MHz; MS at 70 eV; mps are uncorr.; column chromatography and TLC were performed with Si gel. The identity of the known products was established by comparison of their physical data with those of authentic samples. Plant materials were collected at the surroundings of UNICAMP in July 1979, and the fresh aerial parts, ground, percolated with petrol-Et₂O (1:2), concd under red. pres. at room temp. and fractioned by column chromatography (elution: hexane-CHCl₂ and CHCl₂-MeOH).

Extraction of Pterocaulon balansae Chodat. Aerial parts (560 g) of plant (voucher deposited at UEC, No. 2709) afforded successively 27 mg of 7, 1.9 g of 1, 960 mg of 5, 50 mg of 2 and 60 mg of 3.

Extraction of P. lanatum O. Kuntze. Aerial parts (1150 g) of plant (voucher deposited at UEC, No. 2710) afforded successively 15 mg of 1, 85 mg of 6, 3 g of 4, 39 mg of 2 and 50 mg of 3

7-(3-Methyl-2-butenylloxy)-5,6-methylenedioxycoumarin (7). Pale yellow needles, mp 129-30° (Et₂O-petrol) $C_{15}H_{14}O_5$ (Found: C, 65.69; H, 5.14; required: C, 65.37; H, 5.34). Blue fluorescence in UV. UV $\lambda_{\rm max}$ nm (log ε): 313 (3.93), 258 (3.62), 232 (3.99). IR $\nu_{\rm max}$ cm⁻¹: 3050, 1725, 1630, 1585, 855, 822. MS m/z

(rel. int.): 274 (M $^+$, 4), 206 (M $^+$ – C₅H₈, 64), 178 (206 – CO, 64), 69 (C₅H $^+_3$, 100).

7-(2,3-Dihydroxy-3-methylbutylloxy)-5,6-methylenedioxy-coumarin (2). Also prepared from 7-(2,3-epoxy-3-methylbutylloxy)-5,6-methylenedioxy-coumarin (1) via acidic epoxide cleavage according to ref. [8]. Pale yellow needles, mp 160-1° (CHCl₃). $C_{1.5}H_{1.6}O_7$ (Found: C, 58.53; H, 5.30; required: C, 58.44; H, 5.23). [α]_D²⁵ - 12.5° (CHCl₃, c 0.6). Blue fluorescence in UV. UV $\lambda_{\rm max}$ nm (log ϵ): 315 (3.66), 259 (sh, 3.19), 238 (3.58). IR $\nu_{\rm max}$ cm⁻¹: 3600-3200, 1710, 1690, 1580, 980, 940, 860. MS m/z (rel. int.): 308 (M⁺, 0.3), 206 (M⁺ - $C_5H_{10}O_2$, 8), 178 (206 - CO, 59), 59 ($C_3H_7O^+$, 100).

2',3'-Epoxypuberulin (4). Also prepared from 6 by epoxidation according to ref. [9]. Colourless platelets, mp 102-4° (Et₂O-petrol). C₁₆H₁₈O₆ (Found: C, 62.83; H, 5.97; required: C, 62.74; H, 5.92). Blue fluorescence in UV. UV $\lambda_{\rm max}$ nm (log ε): 337 (3.91), 293 (4.10), 226 (4.32). IR $\nu_{\rm max}$ cm $^{-1}$:1720, 1600, 1565, 1245, 965, 870 MS m/z (rel. int.): 306 (M⁺, 30), 222 (M - C₅H₈O, 48), 85 (C₅H₉O⁺, 100). [α] $_D^{25}$ + 98° (CHCl₃, c1.5).

2',3'-Dihydroxypuberulin (8). Also prepared from 2',3'-epoxypuberulin (4). Colourless needles, mp 78-80° (Et₂O). $C_{16}H_{20}O_7$ (Found: C, 59.19; H, 6.20; required: C, 59.25; H, 6.17). Yellow fluorescence in UV. UV λ_{max} nm (log ε): 335 (3.94), 294 (4.08); 225 (4.37). IR ν_{max} cm⁻¹: 3500-3300, 1720, 1610, 1570, 925, 865. MS m/z (rel. int.): 324 (M⁺, 9), 222 (M⁺ - C₅H₁₀O₂, 69), 59 (C₃H₇O⁺, 100). [α]_D²⁵ + 80.6° (CHCl₃, c0.9).

Acknowledgements—We thank the FINEP, Financiadora de Estudos e Projetos, for financial support. R.T.S.F. thanks FAPESP for a fellowship, and S.M.G.B. thanks U.F.Pe. for a leave of absence and CAPES for a fellowship.

RO
OO
OO

3 R =
$$-CH_2-CH(OH)-C(OH)(Me)_2$$
5 R = $-CH_2-CH-C(Me)_2$

MeO

MeO

OMe

$$R = -CH_2 - CH - CH - C(Me)_2$$
 $R = -CH_2 - CH = C(Me)_2$
 $R = -CH_2 - CH(OH) - C(OH)(Me)_2$

REFERENCES

- 1. Cabrera, A. L. and Ragonese, A. M. (1978) Darwiniana 21, 185.
- 2. Bohlmann, F. and Jakupovic, J. (1979) Phytochemistry 18, 1367.
- Johns, R. S., Lamberton, J. A., Price, J. R. and Sioumis, A. A. (1968) Aust. J. Chem. 21, 3079.
- Bohlmann, F., Grenz, M. and Zdero, C. (1975) Chem. Ber. 108, 2955.
- González, A. G., Estevez, R., Arencibia, J. B. and Perez, T. R. (1973) An. Quim. 69, 1141.
- 6. Bohlmann, F. and Zdero, C. (1980) Phytochemistry 19, 331.
- 7. Brown, D., Asplund, R. O. and McMahon, V. A. (1974) *Phytochemistry* 13, 1923.
- Lunnon, M. W. and MacMillan, J. (1977) J. Chem. Soc. Perkin Trans. 1, 2317.
- 9. Paryzek, Z. (1978) J. Chem. Soc. Perkin Trans. 1, 329.