Phytochemistry, Vol 28, No 10, pp 2867–2868, 1989
Printed in Great Britain

0031–9422/89 $3.00+0.00

COUMARINS AND GUAIANOLIDES FROM FURTHER CHILEAN REPRESENTATIVES OF THE SUBTRIBE NASSAUVIINAE

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(*Received* 1 *December* 1988)

Key Word Index—*Nassauvia argentea*, *Proustia ilicifolia* var *baccharoides*, *P. cuneifolia* var *cuneifolia*, *Trichocline caulescens*; Compositae, coumarin derivatives; 5-methyl-4-hydroxycoumarin derivatives, guaianolide glucosides.

Abstract—*Nassauvia argentea* gave two new 5-methyl coumarins both related to nassauvirevolutin C, *Trichocline caulescens* known psoralen derivatives and *Proustia ilicifolia* var. *baccharoides* two known guaianolide-β-D-glucopyranosides and *P cuneifolia* var. *cuneifolia* an isocedrene derivative.

INTRODUCTION

In continuation of our investigations of Chilean representatives of the tribe *Mutisieae* [1], we have now studied three further species from the subtribe Nassauviinae.

RESULTS AND DISCUSSION

The extract of the aerial parts of *Nassauvia argentea* Phil. gave in addition to lupeol and taraxasterol the 5-methyl coumarins **1** [2], **2** and **3**. The structures of **2** and **3** followed from their ^{1}H NMR spectra (Table 1) which were in part close to that of **1** [2]. In particular, the spectrum of **2** was nearly identical with that of **1**, only some chemical shifts and couplings being different. Using NOE difference spectroscopy, the changed configuration at C-2 was established. Thus NOE's between H-14 and H-2 (5%), H-12 and H-10 (6%) as well as between H-15′ and H-2 (4%) were observed.

The ^{1}H NMR spectrum of **3** (Table 1) indicated that here the sesquiterpene moiety was different with a 2,3-double bond and a 7,10-epoxy bridge. The latter followed from the downfield shift of H-14 and the changed coupling pattern of H-10. The data were in part nearly identical with those of the umbelliferone derivative with a corresponding monoterpene with an ether ring [3]. The proposed stereochemistry was deduced from biogenetic considerations as compound **3** is most likely derived from the common precursor of **2** and **3** which has been isolated together with **1** from a *Nassauvia* species [2].

The extract of the aerial parts of *Proustia ilicifolia* H. et A. var. *baccharoides* D. Don. gave in addition to lupeyl and taraxasteryl acetate the guaianolide β-D-glucopyranosides **7** [4, 5] and **8** [5]. Similar guaianolide glucosides have been reported from representatives of the subtribe Gochnatiinae from the genera *Ainsliaea* [6, 7], *Diaspananthus* [8], *Macroclinium* [9] and *Pertya* [10] which all are of East Asian origin

The extract of *P. cuneifolia* D. Don. var. *cuneifolia* gave in addition to flavanoids and triterpenes the isocedrene derivative **9** [11]. Accordingly, the chemistry shows much less variations than *P. cuneifolia* var. *mendocina* [11].

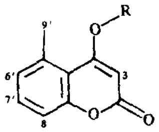
Table 1 ^{1}H NMR spectral data of compounds **2** and **3** (400 MHz, $CDCl_3$, δ-values)

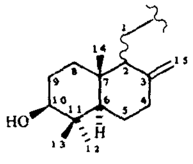
H	**2**	**3**
1	4.39 *dd*	4.65 *br d*
1′	4.18 *dd*	
2	2.33 *br dd*	5.52 *br t*
10	3.26 *dd*	3.74 *d*
12	1.06 *s*	1.06 *s*
13	0.82 *s*	1.02 *s*
14	1.02 *s*	1.33 *s*
15	4.86 *t*	1.76 *br s*
15′	4.75 *t*	
3′	5.69 *s*	5.65 *s*
6′	7.01 *br d*	7.02 *br d*
7′	7.37 *t*	7.37 *t*
8′	7.17 *br d*	7.17 *br d*
9′	2.65 *s*	2.66 *s*

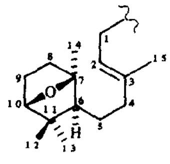
J [Hz]: 6′,7′ = 7′,8′ = 8; compound **2**: 1,1′ = 10; 1,2 = 5; 1′,2 = 8; 2,15 = 2,15′ = 3,15 = 3,15′ = 1.5, 9,10 = 7; 9′,10 = 9, compound **3**: 1,2 = 6.5; 9,10 = 5.

The extract of the aerial parts of *Trichocline caulescens* Phil. gave the psoralen derivatives **4a–4f**, also present in other species of this genus [12], as well as the 5-methyl coumarin **5** [13] and tremetone (**6**).

The results indicated again that 5-methyl coumarins are characteristic for the subtribe Nassauviinae as are isocedrenes. As discussed previously [14], the placement of the Mutisieae in the four subtribes is still not completely solved. It is interesting to note that the glucosides **7** and **8** have been isolated from a *Brachylaena* species [5],

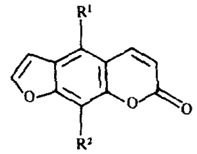




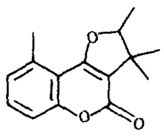


1 2αH
2 2βH

3



	4a	**4b**	**4c**	**4d**	**4e**	**4f**
R¹	H	H	H	H	OMe	ODA
R²	H	OH	OMe	ODA*	H	H



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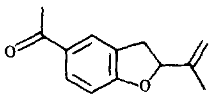

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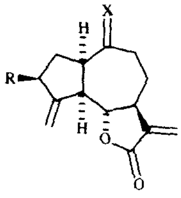
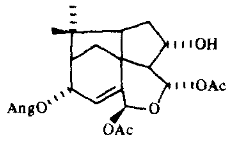
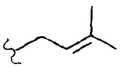




	7	**8**
R	OGlc	H
X	CH₂	βMe,OGlc

9

*DA =



as the position of this genus is in question. A proposed relationship to Mutisieae [15] may be supported by this fact

EXPERIMENTAL

The air-dried plant material (vouchers are deposited in the Herbarium of the University of Concepcion, Chile) was extracted with MeOH–Et_2O–petrol (1:1:1) The extract was worked-up and separated as reported previously [16]

The extract of *Nassauvia argentea* (36 g, aerial parts, collected in January 1988 in Chile, IX region, Volcan Lonquimay, voucher 1869) gave by CC and TLC 10 mg lupeol, 10 mg taraxasterol, 2 mg **1**, 2.5 mg **2** (TLC Et_2O–petrol, 3:1, 6 ×, R_f 0.62) and 6.5 mg **3** (TLC Et_2O–petrol, 3:2, R_f 0.65)

The extract of 815 g aerial parts of *Proustia ilicifolia* (collected in Chile near Copiapo in September 1985, voucher M Rozas 622) gave by CC, TLC and HPLC (RP8, MeOH–H_2O, 11:9) 3.2 mg **8** (R_t 7.9 min) and 6.5 mg **7** (R_t 9.1 min). The extract of the aerial parts of *P cuneifolia* (158 g, collected near La Serena, Chile, I region, Provincia de Arica, voucher Matthei-Rodrigùez TLC a mixture of triterpenes, 17 mg acacetin-7-methyl ether, 8 mg sakuranetin, 7 mg *iso*-sakuranetin and 18 mg **9**

The aerial parts (245 g) of *Trichocline caulescens* (collected in Chile, I region, Provincia de Arica, voucher Matthei-Rodriguez 335) gave by CC and TLC 5 mg psoralen, 3 mg 9-methoxy and 2 mg 9-hydroxypsoralen, 9 mg 5,9-dimethoxypsoralen, 18 mg bergapten, 11 mg imperatorin, 23 mg *iso*-imperatorin, 8 mg **5** and 15 mg **6**.

Dasyphyllum diacanthoides (Less) Cabr (77 g) only gave lupeol and its acetate as well as thymol derivatives

Known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material

2-epi-*Nassauvirevolutin C* (**2**) Colourless gum, IR$\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1} 3520 (OH), 1710, 1615 (coumarin), CIMS m/z (rel int.) 397 $[M+1]^+$ (62) $(C_{25}H_{32}O_4+1)$, 279 (34), 203 (45), 177 (74), 85 (100), MS m/z (rel. int) 220 $[C_{15}H_{24}O]^+$ (4), 202 $[220-H_2O]^+$ (4), 184 $[202-C_2H_4]^+$ (56), 69 $[C_5H_9]^+$ (100), $[\alpha]_D^{24^\circ}-4$ ($CHCl_3$, c 0.08)

7,10-*Epoxy-7,14-dihydronassauvirevolutin A* (**3**) Colourless gum; IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1} 1715, 1620 (coumarin), CIMS m/z (rel.int) 397 $[M+1]^+$ (21) $(C_{25}H_{32}O_4+1)$, 221 (72), 203 (100), $[\alpha]_D^{24^\circ}-13$ ($CHCl_3$, c 0.6)

Acknowledgements—M.S. thanks the Volkswagen Stiftung and the Fondo Nacional de Ciencias de Chile for financial support and M B for an Alexander von Humboldt fellowship

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