Pergamon

PII: S0031-9422(97)00479-2

Phytochemistry, Vol. 46, No. 8, pp. 1393–1395, 1997

Printed in Great Britain
0031-9422/97 $17.00+0.00

COUMARINS FROM *NASSAUVIA CUMINGII*

M. HOENEISEN,* M. SILVA and J. JAKUPOVIC†

Universidad de Concepción, Casilla 2407, Apartado 10, Concepción, Chile; † Institute for Organic Chemistry, Technical University of Berlin, D-10623 Berlin, Str. des 17. Juni 135, Germany

(*Received in revised form* 23 *April* 1997)

Key Word Index—*Nassauvia cumingii*; Asteraceae; 5-methyl coumarins.

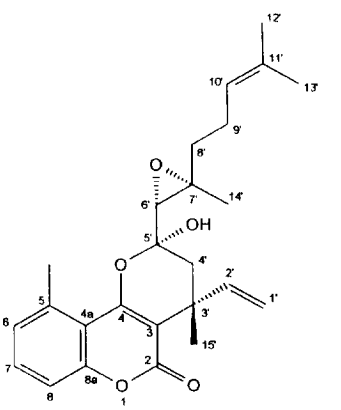
Abstract—The aerial parts of *Nassauvia cumingii* gave a new phenolic compound, presumably derived from a coumarin. The complete relative configuration of a known coumarin was established. © 1997 Elsevier Science Ltd

INTRODUCTION

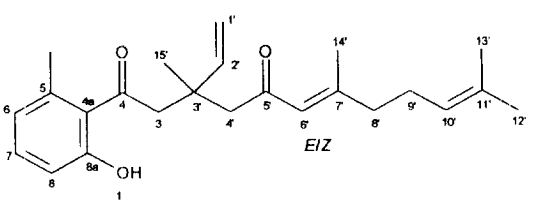
The genus *Nassauvia* is placed in the subtribe Nassauviinae and is represented by 37 species distributed in the Andes from southern Bolivia to Tierra del Fuego and the Malvinas Islands [1]. In Chile, there are 24 species, 10 of which have been investigated chemically [2–8]. As many other genera of the tribe, they are characterized by the occurrence of isocedrenes and 4-hydroxy-5-methyl coumarins. Continuing with our studies of Chilean Asteraceae, we have now examined *N. cumingii*.

RESULTS AND DISCUSSION

The aerial parts of *N. cumingii* H. et A afforded the coumarin **1**, the phenolic compound **2E** and the diterpene **3**. The coumarin has already been described as a constituent of *Triptilion benaventei* [2] and of *N. digitata* [4]. The relative stereochemistry within the cyclic part and in the side-chain was correctly assigned. However, due to free rotation of the side-chain, two diastereomers are possible which would fit the spectral data. Detailed NOE investigation (Table 1) now allowed complete assignment of the relative stereochemistry. In the ^{1}H NMR spectrum (Table 1), the proton of the hydroxyl group appeared as a doublet due to a ^4J long-range coupling with the axial H-4′ (a consequence of the W-in the plane-orientation of the four bonds). Within the side-chain, the configuration of the epoxide ring was deduced from a NOE effect between H-6′ (epoxide proton) and H-8′

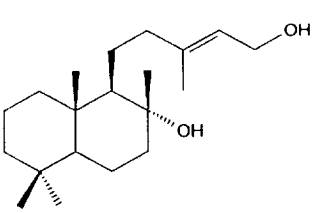


1



2E **2Z**

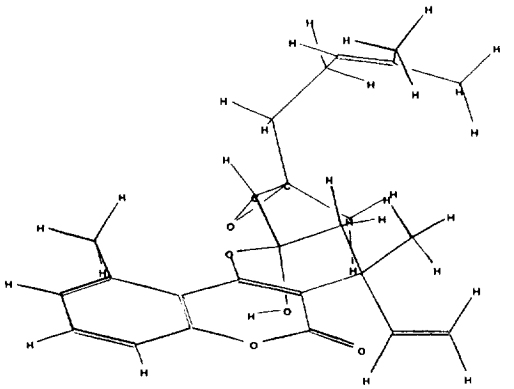
$\Delta^{6'}E$ $\Delta^{6'}Z$



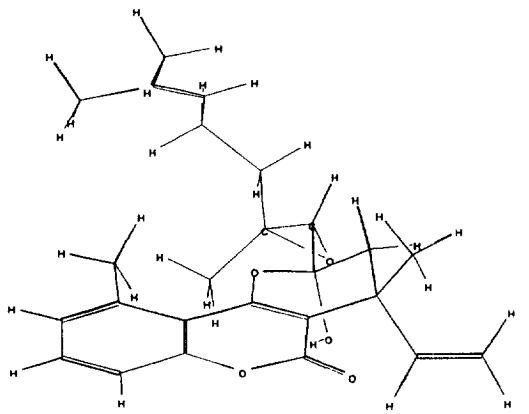
3

* Author to whom correspondence should be addressed.

Murata, H., Lu, S.-T. and Furukawa, H., *Chemical and Pharmaceutical Bulletin*, 1983, **31**, 2879.
16. Yakushijin, K., Tohshima, T., Kitagawa, E., Suzuki, R., Sekikawa, J., Morishita, T., Murata, H., Lu, S.-T. and Furukawa, H., *Chemical and Pharmaceutical Bulletin*, 1984, **32**, 11.
17. Yakushijin, K., Furukawa, H. and McPhail, A. T., *Chemical and Pharmaceutical Bulletin*, 1984, **32**, 23.
18. Fukuyama, Y., Shida, N., Sakurai, T. and Kodama, M., *Phytochemistry*, 1992, **31**, 3975.
19. Fukuyama, Y., Okamoto, K., Shida, N. and Kodama, M., *Chemical and Pharmaceutical Bulletin*, 1994, **42**, 2199.
20. Fukuyama, Y., Shida, N., Hata, Y. and Kodama, M., *Phytochemistry*, 1994, **36**, 1497.
21. Fukuyama, Y., Shida, N., Kodama, M., Chaki, H. and Yugami, T., *Chemical and Pharmaceutical Bulletin*, 1995, **43**, 2270.



1a



1b

Fig. 1. Calculated conformations of diastereomers **1a** and **1b**; the view from bottom to top of the coumarin part. In both structures the zig-zag (W)-orientation of the hydroxyl proton and the axial proton in the pyrane part, as well as the close spacial proximity of the hydroxyl group and the epoxide oxygen leading to a strong hydrogen bonding, is clearly visible. Only the structure **1a** is in accordance with NOE results.

Compound **1**. MS: *m/z* (rel. int.) 410.209 $[M]^+$ (5) (calcd for $C_{25}H_{30}O_5$ 410.209), 271 [M-side-chain]$^+$ (25), 228 [RDA]$^+$ (100), 135 [ArCO]$^+$ (55), 95 (45).

Compounds **2E** *and* **2Z**. MS: *m/z* (rel. int.) 368.236 $[M]^+$ (45) (cald for $C_{24}H_{32}O_3$ 368.235), 350 $[M\text{-}H_2O]^+$ (70), 245 $[M\text{-}C_9H_{15}]^+$ (45), 233 [M-Ar*CO]$^+$ (15), 219 $[M\text{-}ArCOCH_2]^+$ (70), 203 $[M\text{-}C_9H_{15}COCH_2]^+$ (90), 187 (70), 151 $[C_9H_{15}CO]^+$ (75), 149 $[ArCOCH_2]^+$ (55), 135 [ArCO]$^+$ (100), 123 $[C_9H_{15}]^+$ (45), 69 $[C_5H_9]^+$ (60), *Ar = $C_6H_3(OH)(CH_3)$.

Acknowledgements—We thank Fondecyt Project no. 1941106, DAAD and Dirección de Investigación Project no. 9411108-1 Universidad de Concepción, Chile, and Fabiola Rios for technical assistance.

Table 2. ^{1}H NMR data of compounds **2E/Z** and ^{13}C NMR data of compound **2E**

H	**2E** (Δ^6E)	**2Z** (Δ^6Z)	C	**2E** (Δ^6E)
3	3.24 *s*	3.23 *s*		
6	6.69 *br d*	6.69 *br d*	3	51.8 *t*
7	7.19 *dd*	7.19 *dd*	4	207.9 *s*
8	6.78 *br d*	6.78 *br d*	4a	125.3 *s*
9	2.47 *br s*	2.47 *br s*	5	132.5 *s*
1′c	4.97 *d*	4.96 *d*	6	122.9 *d*
1′t	4.96 *d*	4.95 *d*	7	132.8 *d*
2′	6.01 *dd*	6.01 *dd*	8	115.7 *d*
$4'_1$	2.84 *d*	2.82 *d*	8a	159.1 *s*
$4'_2$	2.78 *d*	2.74 *d*	9	23.0 *q*
6′	6.02 *br s*	6.02 *br s*	1′	111.5 *t*
8′	2.10 *m*	2.54 *t*	2′	145.9 *d*
9′	2.10 *m*	2.10 *m*	3′	39.5 *s*
10′	5.05 *m*	5.11 *br t*	4′	51.9 *t*
12′	1.68 *br s*	1.66 *br s*	5′	200.9 *s*
13′	1.60 *br s*	1.59 *br s*	6′	124.6 *d*
14′	2.08 *d*	1.83 *d*	7′	158.6 *s*
15′	1.24 *s*	1.24 *s*	8′	41.3 *t*
OH	10.32 *br s*	10.35 *br s*	9′	26.1 *t*
			10′	123.0 *d*
			11′	137.4 *s*
			12′	25.6 *q*
			13′	17.7 *q*
			14′	19.5 *q*
			15′	25.5 *q*

J(Hz): 6,7 = 7,8 = 8; 1′c,2 = 10.5; 1′t,2 = 17.5; $4'_1$,$4'_2$ = 15.5; 6′,14 = 1; comp. **2Z**: 8′,9′ = 9′,10′ = 7.5;

REFERENCES

1. Cabrera, A. L., *Darwiniana*, 1982, **24**, 283.
2. Bittner, M., Jakupovic, J., Bohlmann, F., Grenz, M. and Silva, M., *Phytochemistry*, 1988, **27**, 3263.
3. Zdero, C., Bohlmann, F., King, R. M. and Robinson, H., *Phytochemistry*, 1986, **25**, 2873.
4. Pritschow, P., Jakupovic, J., Bohlmann, F., Bittner, M. and Niemeyer, H. M., *Phytochemistry*, 1991, **30**, 893.
5. Bittner, M., Jakupovic, J., Bohlmann, F. and Silva, M., *Phytochemistry*, 1989, **28**, 2867.
6. Bittner, M., Silva, M., Rozas, Z., Papastergiou, F. and Jakupovic, J., *Phytochemistry*, 1994, **36**, 695.
7. Bittner, M., Jakupovic, J., Bohlmann, F. and Silva, M., *Phytochemistry*, 1988, **27**, 3845.
8. Zdero, C. and Bohlmann, F., *Plant Systematics and Evolution*, 1990, **171**, 1.
9. Zdero, C., Bohlmann, F., King, R. M. and Robinson, H., *Phytochemistry*, 1986, **25**, 509.