

and S. Kokkini of the Department of Botany, University of Thessaloniki. The aerial parts of the plant, at the flowering state, were air-dried, then 200 g of plant material was subjected to steam distillation in an all-glass assembly for 2 hr yielding 3.2% of essential oil.

**GC/MS analysis.** Analysis and identifications were carried out using a computerized GC/MS. Gas chromatographic separations were performed on a W WCOT SP-2100 column, 30 m, with about 95 000 theoretical plates. He flowed at 1.8 ml/min, temp. 70–270° at 6°/min. The detectors FID and TCD were operated simultaneously after 1:100 split ratio. Mass spectra were taken every 0.6 sec over the range  $m/z$  34–420, utilizing an ionizing voltage of 70 eV.

**Acknowledgements**—We are grateful to Dr. G. Pavlidis and S. Kokkini, Department of Botany, Aristotle University of Thessaloniki, Hellas, for the collection and identification of plant material.

## REFERENCES

1. Guenther, E. (1952) *The Essential Oils*, p. 957. D. Van Nostrand, New York.
2. Anon. (1889) *Semi-Ann. Rept. Oct.* 56.
3. Carvalho Fernandes Costa, A. J. (1945) *Ph.D. thesis, University of Coimbra, Portugal.*
4. Castello-Branco, Mda A. deA. (1952) *Not. Farm.* **18**, 188.
5. Skrubis, B. G. (1972) *Flavour Ind.* **3**, 566, 571.
6. Mateo, C., Morera, M. P., Sanz, J., Calderon, J. and Hernandez, A. (1978) *Riv. Ital. Essenze, Profumi, Piante Off., Aromat, Syndets, Saponi, Cosmet. Aerosols* **60**, 621.
7. Sendra, J. M. and Cunat, P. (1980) *Phytochemistry* **19**, 89.
8. Papageorgiou, V. P. (1980) *Planta Med. Suppl.*, 29.

*Phytochemistry*, Vol. 20, No. 9, pp. 2297–2298, 1981.  
Printed in Great Britain.

0031-9422/81/092297-02 \$02.00/0  
© 1981 Pergamon Press Ltd.

## THREE EUDESMANOLIDES FROM *PLUCHEA ROSEA*\*

XORGE A. DOMINGUEZ, RAUL FRANCO, GERONIMO CANO, ROMELIA VILLARREAL,  
MARINGANTI BAPUJI† and FERDINAND BOHLMANN†

Instituto Tecnológica y de Estudios Superiores de Monterrey, Mexico; † Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany

(Received 13 January 1981)

**Key Word Index**—*Pluchea rosea*; Compositae; sesquiterpene lactones; eudesmanolides.

**Abstract**—Three eudesmanolides of *Pluchea rosea* were found to be structurally related to the eudesmane, cauthemone, earlier reported from plants of the same genus.

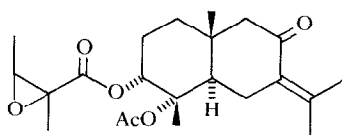
So far, the investigations of *Pluchea* species (Compositae, tribe Inuleae) have shown that eudesmane derivatives like cauthemone (**1**) are characteristic [1–5]. The aerial parts of *Pluchea rosea* Godfrey also afforded **1**. Furthermore, lactones were present in small amounts, the eudesmanolides **2**–**4**. The structures followed from the <sup>1</sup>H NMR data (Table 1). From the spectra of **2** and **3** the presence of an axially orientated ester group at C-3 could be deduced; its nature also followed from the typical <sup>1</sup>H NMR signals. The difference in the chemical shift of H-3 in the spectra of **2** and **3** is characteristic [2, 4] and is obviously due to the deshielding effect of the 4 $\alpha$ -acetoxy group. As the signals of H-5 and H-6 could also be assigned unambiguously, the

presence of an 8,12-lactone was obvious too. The chemical shift of H-9 and of H-13 further supported the proposed structures. The spectrum of **4** (Table 1) was very similar to that of **3**. However, the olefinic singlet at 5.49 ppm was missing. As already clear from the molecular formula, an additional hydroxy group was present, which only could be placed at C-8, most probably  $\beta$ -orientated, as the chemical shift of H-14 obviously was influenced by a deshielding effect of the hydroxyl. Again, the 3 $\alpha$ -orientated ester group clearly followed from the couplings observed. The 8,9-dihydro compound of **2** we have named ixtlixochilin.

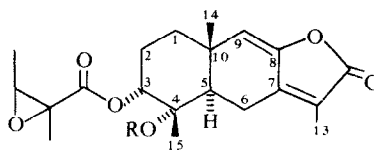
\*Part 364 in the series 'Naturally Occurring Terpene Derivatives'. For Part 363 see Bohlmann, F., Singh, P., Borhtakur, N. and Jakupovic, J. (1981) *Phytochemistry* **20**, (in press).

## EXPERIMENTAL

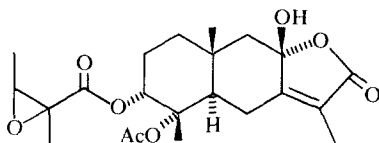
The Soxhlet extract (petrol) of the air-dried aerial parts (2 kg) (Voucher 7733) afforded after column chromatography (Si gel) and TLC (Si gel) 5 mg **1**, 3 mg **2**, 10 mg **3** and 3 mg **4** (separated



1



2 R = H    3 R = Ac



4

with Et<sub>2</sub>O–petrol, 3:1 and HPLC (reversed phase, MeOH–H<sub>2</sub>O, 7:3).

8,9-Dehydroixtlixochilin (2). Colourless gum, IR  $\nu_{\text{max}}^{\text{CCl}_4}$  cm<sup>-1</sup>:

Table 1. <sup>1</sup>H NMR spectral data of compounds 2–4 (400 MHz, CDCl<sub>3</sub>, TMS as internal standard)

	2	3	4
H-3 $\beta$	4.89 <i>br dd</i>	5.88 <i>dd</i>	5.85 <i>dd</i>
H-5 $\alpha$	2.12 <i>dd</i>	2.36 <i>dd</i>	2.02 <i>dd</i>
H-6 $\alpha$	3.04 <i>dd</i>	2.93 <i>dd</i>	2.89 <i>dd</i>
H-6 $\beta$	2.40 <i>br dd</i>	2.45 <i>br dd</i>	2.35 <i>br dd</i>
H-9	5.52 <i>s</i>	5.49 <i>s</i>	1.57 <i>m</i>
H-13	1.92 <i>d</i>	1.95 <i>d</i>	1.89 <i>d</i>
H-14	1.10 <i>s</i>	1.11 <i>s</i>	1.25 <i>s</i>
H-15	1.56 <i>s</i>	1.52 <i>s</i>	1.52 <i>s</i>
OCOR	3.05 <i>q</i> 1.32 <i>d</i> 1.58 <i>s</i>	3.02 <i>q</i> 1.29 <i>d</i> 1.62 <i>s</i>	3.05 <i>q</i> 1.29 <i>d</i> 1.61 <i>s</i>
OAc	—	2.00 <i>s</i>	2.00 <i>s</i>

*J*(Hz): Compounds 2 and 3: 2 $\alpha$ ,3 $\beta$  = 2.5; 5 $\alpha$ ,6 $\alpha$  = 2.5; 5 $\alpha$ ,6 $\beta$  = 13.5; 6 $\alpha$ ,6 $\beta$  = 16; 6 $\beta$ ,13 = 1.5; 3',4' = 5; compound 4: 2 $\alpha$ ,3 $\beta$  = 2.5; 5 $\alpha$ ,6 $\alpha$  = 2.5; 5 $\alpha$ ,6 $\beta$  = 13.5; 6 $\alpha$ ,6 $\beta$  = 16; 6 $\beta$ ,13 = 1.5; 3',4' = 5.

3500 (OH), 1770, 1665 ( $\gamma$ -lactone), 1740 (CO<sub>2</sub>R); MS *m/z* (rel. int.): 362.173 (M<sup>+</sup>, 4) (C<sub>20</sub>H<sub>26</sub>O<sub>6</sub>), 344 (M – H<sub>2</sub>O, 1), 333 (M – CHO, 20), 228 (344 – RCO<sub>2</sub>H, 25), 213 (228 – Me, 10), 99 (RCO<sup>+</sup>, 10), 71 (99 – CO, 67), 55 (C<sub>4</sub>H<sub>7</sub><sup>+</sup>, 100).

8,9-Dehydroixtlixochilin-4-O-acetate (3). Colourless gum, IR  $\nu_{\text{max}}^{\text{CCl}_4}$  cm<sup>-1</sup>: 1780 ( $\gamma$ -lactone), 1745 (OAc, CO<sub>2</sub>R); MS *m/z* (rel. int.): 404.183 (M<sup>+</sup>, 0.5) (C<sub>22</sub>H<sub>28</sub>O<sub>7</sub>), 344 (M – HOAc, 8), 228 (344 – RCO<sub>2</sub>H, 100), 213 (228 – Me, 56), 99 (RCO<sup>+</sup>, 28), 71 (99 – CO, 81).

$$[\alpha]_{24}^{\text{D}} = \frac{589}{+109} + \frac{578}{+115} + \frac{546}{+132} + \frac{436 \text{ nm}}{+234} \quad (c = 0.7, \text{CHCl}_3).$$

8 $\beta$ -Hydroxyixtlixochilin-4-O-acetate (4). Colourless gum, IR  $\nu_{\text{max}}^{\text{CCl}_4}$  cm<sup>-1</sup>: 1780 (lactone), 1740 (OAc, CO<sub>2</sub>R); MS *m/z* (rel. int.): 422.194 (M<sup>+</sup>, 3) (C<sub>22</sub>H<sub>30</sub>O<sub>8</sub>), 362 (M – HOAc, 10), 344 (362 – H<sub>2</sub>O, 2), 228 (344 – RCO<sub>2</sub>H, 23), 99 (RCO<sup>+</sup>, 12), 71 (99 – CO, 100).

*Acknowledgements*—X.A.D. thanks Syntex of Mexico, S.A. for financial support and for a CONACYT grant (C04-70).

## REFERENCES

- Chiang, M. T., Bittner, M., Silva, M., Watson, W. H. and Sammes, P. G. (1979) *Phytochemistry* **18**, 2033.
- Bohlmann, F. and Mahanta, P. K. (1978) *Phytochemistry* **17**, 1189.
- Bohlmann, F. and Zdero, C. (1976) *Chem. Ber.* **109**, 2653.
- Bohlmann, F., Ziesche, J., King, R. M. and Robinson, H. (1980) *Phytochemistry* **19**, 905.
- Nakanishi, K., Croud, R., Miura, I., Dominguez, X., Zamudio, A. and Villarreal, R. (1974) *J. Am. Chem. Soc.* **96**, 609.