Phytochemistry, Vol. 20, No. 6, pp. 1417–1418, 1981.
Printed in Great Britain.

0031-9422/81/061417-02 $02.00/0

PROSTAGLANDIN-LIKE FATTY ACID DERIVATIVE FROM *CHROMOLAENA MORII*

FERDINAND BOHLMANN, RAJINDER K. GUPTA, ROBERT M. KING* and HAROLD ROBINSON*

Institute for Organic Chemistry, Technical University Berlin, D-1000 Berlin 12, West Germany; *Smithsonian Institution, Washington, DC 20560, U.S.A.

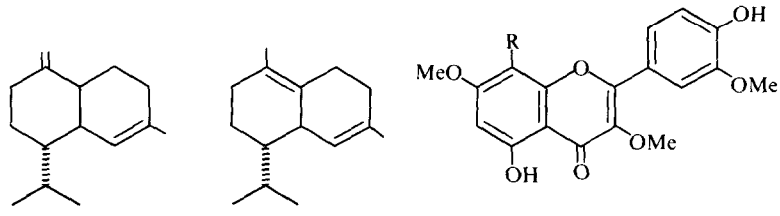
(*Received* 16 *September* 1980)

Key Word Index—*Chromolaena morii*; Compositae; cyclic fatty acid derivative.

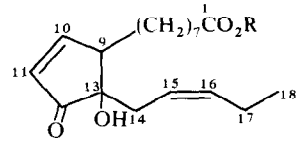
The aerial parts of *Chromolaena morii* K. et. R. (tribe Eupatorieae, Compositae) afforded germacrene D, γ-humulene, caryophyllene, bicyclogermacrene, squalene, the cadinenes **1** and **2**, the flavonols **3** [1] and **4** [2] as well as the acid **5**, which was purified as its methyl ester **6**. Periodate cleavage of **6** gave the keto acid **7**, which was transformed to the dimethyl ester **8**. Most of the ^{1}H NMR data of **5** and its derivatives could be assigned by spin decoupling. The presence of the sequence H-14 to H-18 followed from the results of the decoupling of the signals of the olefinic protons (δ = 5.58 and 5.32). Irradiation at 2.86 ppm decoupled the signals of H-10 and H-11, which showed a 6 Hz vicinal coupling with each other indicating a double bond in a five-membered ring. The position of the keto group followed from the downfield shift of the 10-H signal, while the position of the hydroxyl group could be deduced indirectly by the missing couplings of 14-H. These assignments were established by the ^{1}H NMR spectrum of **8**, which allowed a clear decision to be made as to the relative position of the substituents at C-9 and C-13. The ^{13}C NMR data of **6** also supported the structure, while the mass spectrum showed the expected fragments: M − $^{\cdot}CH_2$ $CH{=}CHCH_2Me$ and M − $^{\cdot}(CH_2)_7CO_2Me$. The configurations at C-9 and C-13 could not be determined. We have named **5** chromomoric acid. Probably **5** is formed from linolenic acid, in a similar way to the formation of the prostagladins from arachidonic acid, through **9** and **10**. The latter has been reported as a product from the incubation of linolenic acid with a flaxseed extract [3]. The roots gave germacrene D, γ-humulene, caryophyllene and bicyclogermacrene. Only the cadimenes **1** and **2** may be typical for a *Chromolaena* species. Several oxygenated derivatives have been isolated from other species (see [4] and references cited therein).

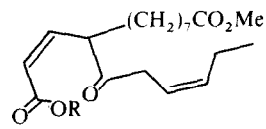
EXPERIMENTAL

The air-dried plant material (voucher RMK 8067) was extracted with Et_2O–petrol (1:2). The resulting extracts were separated by CC (Si gel) and TLC (Si gel). The roots (100 g)

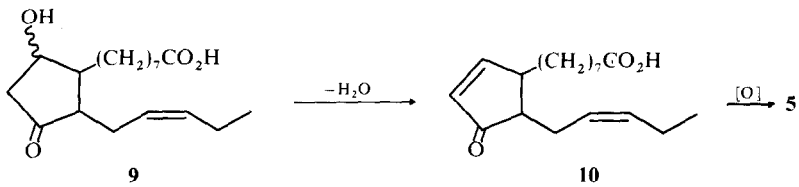


1 **2** **3** R = H **4** R = Me





5 R = H **6** R = Me **7** R = H **8** R = Me



9 **10**

afforded 20 mg germacrene D, 20 mg γ-humulene, 10 mg caryophyllene and 10 mg bicyclogermacrene, while the aerial parts (450 g) gave 100 g germacrene D, 50 mg γ-humulene, 50 mg caryophyllene, 20 mg bicyclogermacrene, 200 mg squalene, 10 mg **1**, 10 mg **2**, 50 mg **3**, 100 mg **4** and 20 mg **5** (Et_2O–petrol, 3:1). **5** was obtained as a colourless gum, which was esterified with CH_2N_2 to give **6** as a colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3550 (OH), 1740 (CO_2R), 1720 (C=O); MS *m/z* (rel. int.) 322.214 (M^+, 4) ($C_{19}H_{30}O_4$), 304 (M − H_2O, 4), 291 (M − ·OMe, 7), 253.144 (M − ·CH_2CH=CHEt, 61) ($C_{14}H_{21}O_4$), 221 (253 − MeOH, 100), 165 (M − ·$(CH_2)_7$ CO_2Me, 28), 147 (165 − H_2O, 15), 69 ($C_5H_9^+$, 41).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+67 \quad +69 \quad +80 \quad +146} \qquad (c = 0.8,\ CHCl_3).$$

^{13}C NMR ($CDCl_3$): δ 208.5 (C-12) 174.2 (C-1), 164.2 (C-10), 136.3 (C-15), 130.1 (C-16), 121.5 (C-11), 80.7 (C-13), 52.0 (OMe), 51.4 (C-9), 34.1, 32.5, 29.5, 29.1, 28.2, 27.9, 25.0, 20.7 (CH_2), 14.0 (C-18). To 5 mg **6** in 1 ml MeOH 15 mg $NaIO_4$ were added. After 2 hr, **7** (2 mg) was isolated by TLC(Et_2O) as a colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2600, 1735 (CO_2H), 1735 (CO_2R), 1690 (C=CCO). Addition of CH_2N_2 gave **8**, colourless gum, MS *m/z* (rel. int.): 352 (M^+, 1), 321 (M − ·OMe, 10), 283 (M − C_5H_9, 18), 251 (283 − MeOH, 72), 69 ($C_5H_9^+$, 100).

Acknowledgements—We thank Drs. Scott A. Mori and P. Alvim, Herbario Centro de Pesquisas at Itatanu, Bahia, Brazil, for their help during plant collection and the Deutsche Forschungsgemeinschaft for financial support.

Table 1. ^1H NMR data of compounds **6**–**8** (270 MHz, $CDCl_3$, TMS as internal standard)

	6	**7**	**8**
H-2	2.31 *t*	2.32 *t*	2.32 *t*
H-3, H-8	1.65 *m*	1.65 *m*	1.65 *m*
H-4, H-7	1.36 *m*	1.33 *m*	1.33 *m*
H-9	2.86 *m*	3.30 *m*	3.29 *m*
H-10	7.54 *dd*	6.3 *m*	6.15 *dd*
H-11	6.18 *dd*	6.1 *d* (*br*)	5.93 *dd*
H-14	2.50 *dd* (*br*)	3.3 *m*	3.29 *m*
H-14′	2.14 *dd* (*br*)		
H-15	5.58 *ddd* (*br*)	5.55 *m*	5.55 *m*
H-16	5.32 *dt* (*br*)		
H-17	2.04 *dq* (*br*)	2.05 *dq* (*br*)	2.03 *dq* (*br*)
H-18	0.96 *t*	0.97 *t*	0.98 *t*
OMe	3.67 *s*	3.67 *s*	3.67 *q*

J (Hz): **6**: 2, 3 = 7.5; 9, 10 = 2; 9, 11 = 2; 10, 11 = 6.5; 14, 14′ = 14.5; 14, 15 = 8; 14′, 15 = 6; 15, 16 = 11; 16, 17 = 17, 18 = 7; **8**: 9, 10 = 10; 9, 11 = 2; 10, 11 = 11.

REFERENCES

1. Fraser, A. W. and Lewis, J. R. (1973) *Phytochemistry* **12,** 1787.
2. Fukui, K. and Matsumoto, T. (1965) *J. Chem. Soc. Jpn, Pure Chem. Sect.* **86,** 1079.
3. Zimmermann, D. C. and Feng, P. (1978) *Lipids* **13,** 313.
4. Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1979) *Phytochemistry* **18,** 1177.