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FURTHER PROSTAGLANDIN-LIKE FATTY ACIDS FROM *CHROMOLAENA MORII*

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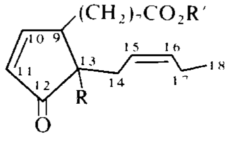
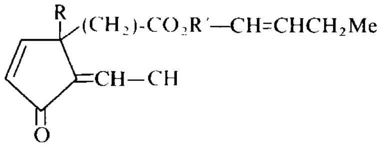
Key Word Index—*Chromolaena morii*; Compositae; cyclic fatty acid derivatives; prostaglandin-like acids.

Abstract—A re-investigation of *Chromolaena morii* afforded seven further prostaglandin-like fatty acids.

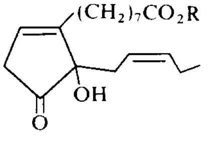
From the aerial parts of *Chromolaena morii* K. et R. (tribe Eupatorieae) a prostaglandin-like fatty acid (**1a**) was isolated [1]. A re-investigation of this plant has now afforded seven further compounds of this type, which were isolated as their methyl esters. From the ^1H NMR data (Table 1) the structures **2b**–**8b** could be deduced. The signals were in part similar to those of **1b**, but some were different, indicating a changed situation of the unsaturated part of the molecules. In the spectrum of **2b**, an additional three-fold doublet at δ 2.00 was that of H-13, as could be shown by spin decoupling. Irradiation at δ 2.3 collapsed the latter to a doublet, while one of the olefinic signals was also altered. Small shift differences of several other signals, if compared with the corresponding ones in the spectrum of **1b**, were due to the absence of a hydroxyl group at C-13. The ^1H NMR data of **3b** and **4b** indicated that anhydro derivatives of **1b** were present. From the different chemical shifts of H-14 and H-15, the stereochemistry of the new double bond was deduced. The couplings of H-15 and H-16 further showed that **3b** was the *cis*- and **4b** the *trans*-isomer. The spectra of **5b**–**7b** (Table 1) showed that again these compounds were isomers. As the H-10 and H-11 signals were now doublets only, the additional hydroxyl group was placed at C-9. The stereochemistry of the 13,14 and 15,16-double bonds again followed from the chemical shifts and the couplings, respectively. Only in the spectrum of **7b** was the H-14 signal shifted downfield due to the deshielding effect of the keto group at C-12, while the coupling $J_{15,16}$ indicated that **5b** was a *cis*-isomer and that **6b** as well as **7b** were *trans*-isomers, though **5b** and **6b** could not be separated. The ^1H NMR data of **8b** (Table 1) indicated that the 10,11-double bond was shifted. Spin decouplings clearly showed that we were dealing with a 9,10-unsaturated isomer. Consequently, a new triplet triplet for H-8 was visible and the H-11 signal was a doublet triplet at δ 2.82. Obviously, all the acids are closely related and are presumably formed from linolenic acid in a similar way to that proposed for the biosynthesis of the prostaglandins [1].



	1a	1b	2a	2b
R	OH	OH	H	H
R′	H	Me	H	Me



	3a	3b	4a	4b	5a	5b	6a	6b	7a	7b
R	H	H	H	H	OH	OH	OH	OH	OH	OH
R′	H	Me	H	Me	H	Me	H	Me	H	Me
13	*Z*	*Z*	*E*	*E*	*E*	*E*	*E*	*E*	*Z*	*Z*
15	*Z*	*Z*	*E*	*E*	*Z*	*Z*	*E*	*E*	*E*	*E*



8a R = H
8b R = Me

Table 1. ^1H NMR spectral data of compounds **2b**–**8b** (400 MHz, $CDCl_3$, TMS as internal standard)

	2b	**3b** (47°)	**4b** (C_6D_6)	**5b**	**6b**	**7b**	**8b**
H-2	2.29 *t*	2.28 *t*	2.14 *t*	2.27 *t*	2.28 *t*	2.27 *t*	2.30 *t*
H-3	1.60 *m*	1.60 *m*	1.55 *m*	1.57 *m*	1.58 *m*	1.57 *m*	1.6 *m*
H-8							2.29 *tt*
H-4–7	1.30 *m*	1.30 *m*	1.35 *m*	1.30 *m*	1.30 *m*	1.33 *m*	1.4–1.3 *m*
H-9	2.57 *ddt*	3.53 *m*	3.20 *m*		—	—	—
H-10	7.58 *dd*	7.50 *dd*	6.93 *dd*	7.23 *d*	7.23 *d*	7.28 *d*	5.87 *tt*
H-11	6.11 *dd*	6.34 *dd*	6.27 *dd*	6.33 *d*	6.27 *d*	6.30 *d*	2.82 *dt*
H-13	2.00 *ddd*	—	—	—	—	—	—
H-14	2.3 *m*	7.25 *d*(*br*)	7.15 *m**	6.89 *brd*	6.54 *brd*	6.29 *d*(*br*)	2.56 *dd* 2.35 *m*
H-15	5.44 *ddd*(*br*)	6.20 *ddt*	6.22 *ddt*	6.64 *ddt*	7.54 *ddt*	6.68 *ddt*	5.5 *ddd*(*br*)
H-16	5.23 *dt*(*br*)	5.96 *dt*	5.85 *dt*	6.04 *dt*	6.19 *dt*	6.26 *dt*	5.11 *dt*
H-17	2.05 *dq*(*br*)	2.37 *dddq*	1.95 *dq*(*br*)	2.38 *dq*(*br*)	2.36 *dq*(*br*)	2.38 *dq*(*br*)	2.03 *dq*(*br*)
H-18	0.94 *t*	1.04 *t*	0.86 *t*	1.04 *t*	1.07 *t*	1.07 *t*	0.93 *t*
OMe	3.67 *s*	3.66 *s*	2.43 *s*	3.65 *s*	3.66 *s*	3.65 *s*	3.67 *s*

* $CDCl_3$ 6.93 *d*(*br*).

J(Hz): 2,3 = 16,17 = 17,18 = 7; 10,11 = 6; compound **2b**: 8,9 = 7; 9,10 = 2.5; 9,11 = 2; 9,13 = 2; 13,14 = 8; 13,14′ = 5; 14,15 = 7; 15,16 = 11; compound **3b**: 9,10 = 2.5; 9,11 = 2; 14,15 = 12; 15,16 = 10; 15,17 = 1.5; compound **4b**: 9,10 = 2.5; 9,11 = 2; 15,17 = 1.5; 14,15 = 10; 15,16 = 15; compound **5b**: 14,15 = 11.5; 15,16 = 15; 15,17 = 1.5; compound **6b**: 14,15 = 11.5; 15,16 = 15; 15,17 = 1.5; compound **7b**: 14,15 = 11; 15,16 = 15; 15,17 = 1.5; compound **8b**: 8,10 = 8,11 = 10,11 = 2; 14,15 = 9; 14′,15 = 6; 14,14′ = 13.5; 15,16 = 10.5; 15,17 = 1.

EXPERIMENTAL

The air-dried aerial parts (voucher RMK 8131) were extracted with Et_2O–petrol (1:2) and the extract was separated by CC (Si gel). The polar fractions were esterified by addition of CH_2N_2 and the resulting esters were separated by repeated TLC (Si gel). With Et_2O–CH_2Cl_2 (1:9), 2 mg **2b** was obtained as a colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745 (CO_2R), 1715 (C=CCO); MS *m/z* (rel. int.): 306.220 $[M]^+$ (10) ($C_{19}H_{30}O_3$), 275 $[M - {}^{\cdot}OMe]^+$ (100), 243 $[275 - CO]^+$ (11). The same solvents gave 3 mg **3b** and 1.5 mg **4b**. **3b**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 1690, 1630 (C=CC=O); MS *m/z* (rel. int.): 304.204 $[M]^+$ (31) ($C_{19}H_{28}O_3$), 275 $[M - C_2H_5]^+$ (100), 273 $[M - {}^{\cdot}OMe]^+$ (12), 243 $[275 - MeOH]^+$ (19), 161 $[M - (CH)_7CO_2Me]^+$ (44); $[\alpha]_D = -5°$ ($c = 0.1$, $CHCl_3$). **4b**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 1700 (C=CC=O); MS *m/z* (rel. int.): 304.204 $[M]^+$ (21), 275 $[M - Et]^+$ (100), 243 $[275 - MeOH]^+$ (19), 161 $[M - {}^{\cdot}(CH_2)_7CO_2Me]^+$ (38); $[\alpha]_D = 20°$ ($c = 0.1$, $CHCl_3$).

With Et_2O–CH_2Cl_2 (3:17), 10 mg **1b** and 2 mg **8b** were obtained as colourless gums, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1735 (CO_2R), 1710 (C=CCO); MS *m/z* (rel. int.): 253.144 $[M - C_5H_9]^+$ (40) ($C_{14}H_{21}O_4$), 221 $[253 - MeOH]^+$ (100), 193 $[221 - CO]^+$ (14); $[\alpha]_D = +7°$ ($c = 0.1$, $CHCl_3$). Separation with Et_2O–CH_2Cl_2–MeOH (15:85:1), gave 3 mg **5b**, 3 mg **6b** (not separated) and 4 mg **7b** as colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R), 1700, 1635 (C=CC=O); MS *m/z* (rel. int.): 320.199 $[M]^+$ (18) ($C_{19}H_{28}O_4$), 302 $[M - H_2O]^+$ (4), 291 $[M - Et]^+$ (40), 259 $[291 - MeOH]^+$ (32), 163 $[M - (CH_2)_7CO_2Me]^+$ (62), 55 $[C_4H_7]^+$ (100);

$$[\alpha]^{\lambda}_{24} = \frac{589 \quad 578 \quad 546 \quad 436\,\mathrm{nm}}{+1 \quad +5 \quad +22 \quad +295} (c = 0.4, \mathrm{CHCl_3}).$$

Mixture of **5b** and **6b**, colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1740 (CO_2R), 1700, 1635 (C=CC=O); MS *m/z* (rel. int.): 320.199 $[M]^+$ (17) ($C_{19}H_{28}O_4$), 302 $[M - H_2O]^+$ (5), 291 $[M - Et]^+$ (12), 259 $[291 - MeOH]^+$ (8), 163 $[M - {}^{\cdot}(CH_2)_7CO_2Me]$ (100).

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