Phytochemistry, 1980, Vol. 19, pp. 2047–2048. Pergamon Press Ltd. Printed in England.

PSEUDOGUAIANOLIDES FROM *WEDELIA GRANDIFLORA**

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(*Received* 7 *December* 1979)

Key Word Index—*Wedelia grandiflora*; Compositae; new pseudoguaianolides.

In addition to the compounds isolated previously [1], a reinvestigation of the aerial parts of *Wedelia grandiflora* Benth. afforded a complex mixture of minute amounts of sesquiterpene lactones, which could not be completely separated. All data are, however, in agreement with the structures **1**–**5**. Acetylation of **1** afforded the acetate **2**. Partial saponification of the diesters **2**–**5** led to the monoesters **6**, indicating that the acetate group was positioned at C-4. As usual, methanol addition at the 11,13-double bond had occurred. The ^{1}H NMR data and the MS of the esters **2**–**5** clearly showed the nature of the ester residues. Decoupling-experiments with **1** established the assignments given in Table 1. Irradiation at δ 3.47 collapsed the doublets at 6.35, 5.87 and 5.89 to singlets and the signal at 4.85 to a doublet of doublets. This clearly indicated that the broadened doublet at 3.47 must be assigned to 7-H. The observed coupling of $J_{7,8}$ further showed that, most probably, the hydrogens at C-7 and C-8 had a *cis* arrangement and that we were dealing with an 8,12-lactone as the chemical shift of 6-H did not agree with a 6,12-lactone. The 6β-orientation of the methacryloyloxy group was indicated by the small coupling of $J_{6,7}$ which would not be in agreement with a 6α-substituted lactone [2]. Also the downfield shift of the 13′-H signal supported this assumption. A Dreiding model shows that the oxygen function at C-4 is also probably β-orientated as the C-5 methyl signal was shifted downfield when compared with the chemical shift in other pseudoguaianolides [2]. However, the 1,10-double bond may be responsible for this shift, and, therefore, the stereochemistry at C-4 is not certain. We have given the name wedelifloride to the diol corresponding to **1**.

The isolation of pseudoguaianolides may indicate a relationship of *Wedelia* to *Helenium* and related genera. In addition to the co-occurence of these lactones thiophene acetylenes are also widespread in both genera [3].

Table 1. ^{1}H NMR spectral data of compounds **1**, **2** and **6** (270 MHz, TMS as internal standard)

	1		**2***	**6**
	($CDCl_3$)	(C_6D_6)	($CDCl_3$)	($CDCl_3$)
2-H	2.13 *t*(*br*)	1.8 *m*	2.2 *m*	2.2 *m*
4-H	3.78 *dd*	3.72 *dd*	4.85 *dd*	3.66 *dd*
6-H	5.89 *d*	5.92 *d*	5.97 *d*	6.01 *d*
7-H	3.47 *d*(*br*)	2.92 *d*(*br*)	3.42 *d*(*br*)	2.88 *m*
8-H	4.85 *ddd*	4.28 *ddd*	4.82 *ddd*	4.87 *ddd*
9-H	2.60 *dd*	2.58 *dd*		
9′-H	1.90 *dd*	1.69 *dd*		
13-H	6.35 *d*	6.19 *d*	6.35 *d* }	3.72 *d*
13′-H	5.87 *d*	5.30 *d*	5.89 *d* }	
14-H	1.67 *s*(*br*)	1.56 *s*(*br*)	1.70 *s*(*br*)	1.81 *s*(*br*)
15-H	1.11 *s*	1.20 *s*	1.21 *s*	1.14 *s*
OAc	—	—	2.06 *s*	—
OMe	6.14 *dq*	6.11 *dq*	6.14 *dq*	6.12 *dq*
	5.65 *dq*	5.26 *dq*	5.65 *dq*	5.62 *dq*
	1.98 *dq*	1.85 *dq*	1.98 *dd*	1.96 *dd*

J (Hz): 2,3 = 7; 3,4 = 9; 3′,4 = 6; 6,7 = 2; 7,8 = 7; 7,13 = 2.5; 7,13′ = 2.2; 8,9 = 4.5; 8,9′ = 9; $3_1{}',3_2{}'$ = 1; 3′,4′ = 1.5.

* The signals of **3**–**5** are nearly the same; *O*-*i*-Bu: 2.59 *qq*, 1.22 *d*; *O*-Tigl: 6.88 *qq*, 1.86 *s*(*br*); *O*-*i*-Val: 2.22 *d*, 0.87 *d*.

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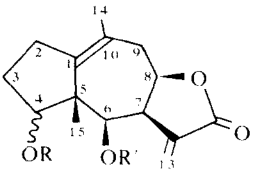
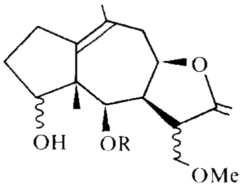
* Part 279 in the series "Naturally Occurring Terpene Derivatives". For part 278 see Bohlmann, F., Dhar, A. K. and Ahmed, M. (1980) *Phytochemistry* **19**, 1850.



	1	**2**	**3**	**4**	**5**
R	H	Ac	Ac	Ac	Ac
R′	Meacr	Meacr	*i*-Bu	Tigl	*i*-Val



6 (R = Meacr, *i*-Bu, Tigl, *i*-Val)

However, as in many other genera of the Heliantheae, kaurene derivatives are also typical for *Wedelia* [1, 4].

EXPERIMENTAL

Air-dried aerial parts (voucher RMK 7870) were chopped (350 g) and extracted with Et_2O–petrol (1:2). The resulting extract was treated with MeOH to remove saturated hydrocarbons. CC (Si gel, act. grade II) and repeated TLC (Si gel GF 254) finally afforded, in addition to the kaurene derivatives previously isolated [1], 17 mg **1** (Et_2O–petrol, 3:1) and 20 mg **2**–**5** (*ca* 4:1:1:1), which could not be completely separated.

Wedelifloride-6-O-methacrylate (**1**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: OH 3620; γ-lactone 1770; $C{=}CCO_2R$ 1715, 1650; MS *m/e* (rel. int.): 332.162 (M^+, 8) ($C_{19}H_{24}O_5$); 314 ($M - H_2O$, 3); 246 ($M - RCO_2H$, 69); 228 ($246 - H_2O$, 32); 202 ($246 - CO_2$, 100); 69 ($C_3H_5CO^+$, 63). 5 mg **1** in 0.5 ml Ac_2O were heated for 1 hr at 70°. TLC afforded 3 mg **2**, ^1H NMR identical with that of the natural compound.

6-O-Methacryloyloxy-, isobutyryloxy-, tiglinoyloxy-, and isovaleryloxy-wedelifloride-4-O-acetate (**2**–**5**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: γ-lactone 1775; OAc, CO_2R 1740; $C{=}CCO_2R$ 1715; MS *m/e* (rel. int.): 328.168 ($M - HOAc$, 1) ($C_{20}H_{24}O_4$), 316.168 (2) ($C_{19}H_{24}O_4$), 314.158 (6) ($C_{19}H_{22}O_4$): 228 ($314 - C_3H_5CO_2H$, 100); 85 ($C_4H_9CO^+$, 5); 83 ($C_4H_7CO^+$, 44); 71 ($C_3H_7CO^+$, 19); 69 ($C_3H_5CO^+$, 73). To 10 mg **2**–**5** in 3 ml MeOH at room temp. was added 0.2 ml 2 N KOH and after 1 hr dil H_2SO_4 was added. TLC afforded 5 mg **6**, colourless gum. ^1H NMR (Table 1).

Acknowledgement—We thank the Deutsche Forschungsgemeinschaft for financial support.

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