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GUAIANOLIDES FROM *AGRIANTHUS PUNGENS**

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Key Word Index -- *Agrianthus pungens*; Compositae; sesquiterpene lactones; guaianolides.

The Brazilian genus *Agrianthus* has not been investigated chemically. Therefore, we have studied the constituents of *A. pungens* Mattf. The roots only afforded the widespread pentayne 1 [1], coumarin (2), and dammaradienyl acetate (4) [2] but the aerial parts yielded in addition to 2 and germacrene D (3) [3] a complex mixture of sesquiterpene lactones, which could be only partly separated. The main compound most probably had the structure 5. The ¹H NMR data (Table 1) were very similar to those reported for graminiliatrin [4], which, however, has another ester function at C-8 and the additional hydroxyl group at C-9 is missing. The 9 α -position of this hydroxyl in 5 was indicated by the observed coupling $J_{8,9}$ and the downfield shift of 1 α -H. Models show that the latter should be deshielded by the 9 α -hydroxy group. The assignments were established by double resonance experiments.

A second lactone, not separated completely from an unidentified lactone, most probably was the corresponding precursor of 5, where the epoxy oxygen at C-3, C-4 is missing. The ¹H NMR data (Table 1) would be in agreement with the structure 6, which we have named agriantholide. The structures of three further lactones

Table 1. ¹H NMR spectral data of compounds 5 and 6 (270 MHz, in CDCl₃ with TMS as internal standard)

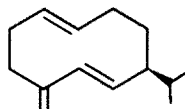
	5	6
1-H	2.27 <i>dd</i>	2.1 <i>m</i>
2-H	3.91 <i>d</i>	4.75 <i>m</i>
3-H	3.42 <i>s</i>	5.68 <i>s(br)</i>
5-H	2.44 <i>dd</i>	2.35 <i>dd</i>
6-H	5.08 <i>dd</i>	5.18 <i>dd</i>
7-H	3.09 <i>dddd</i>	3.22 <i>dddd</i>
8-H	5.62 <i>dd</i>	5.46 <i>dd</i>
9-H	4.38 <i>d</i>	3.99 <i>d</i>
13-H	6.32 <i>d</i>	6.33 <i>d</i>
13'-H	5.52 <i>d</i>	5.48 <i>d</i>
14-H	3.04 <i>d</i>	3.08 <i>d</i>
14'-H	2.75 <i>d</i>	2.85 <i>d</i>
15-H	1.71 <i>s</i>	2.00 <i>s(br)</i>
OCOR	6.89 <i>q(br)</i>	6.89 <i>q(br)</i>
	1.80 <i>d(br)</i>	1.81 <i>d(br)</i>
	1.79 <i>s(br)</i>	1.80 <i>s(br)</i>

$J(\text{Hz})$: 1,2 = 5; 1,5 = 7.5; 5,6 = 10; 6,7 = 9; 7,8 = 2; 7,13 = 3.3; 7,13' = 3; 8,9 = 4.5.

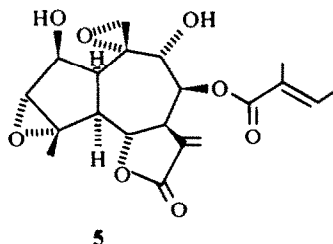
* Part 276 in the series "Naturally Occurring Terpene Derivatives". For Part 275 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1980) *Phytochemistry* 19 (in press).



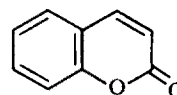
1



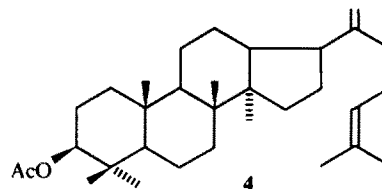
3



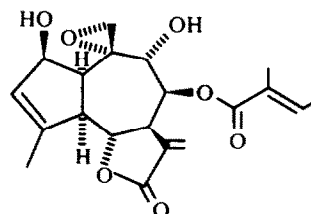
5



2



4



6

present in very minute amounts could not be established. At least two are most probably closely related guaianolides.

The compounds isolated from the *Agrianthus* species may be chemotaxonomically useful. However, so far not enough data from other genera of the *Gyptis* group [5] are available for clear conclusions. Up to now there are only results on *Conocliniopsis* [5], where heliangolides are present, and on *Conoclinium* [6–8], which only afforded simple compounds. Both are also placed in the *Gyptis* group [9].

EXPERIMENTAL

The air-dried plant material (voucher No. RMK 8100), collected in north-eastern Brazil, was chopped and extracted with Et₂O–petrol (1:2) and the resulting extracts were first separated by CC (Si gel, act. grade II) and further by TLC (Si gel GF 254). Roots (60 g) afforded 0.1 mg 1, 1 mg 2 and 3 mg 4, while 200 g of arial parts yielded 8 mg 2, 5 mg 3, 10 mg 5 (Et₂O–MeOH, 50:1) and 3 mg 6 (Et₂O–MeOH, 50:1).

3,4,4α-Epoxyagriantholide (5). Colourless gum, IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3600 (OH), 1770 (lactone), 1720, 1650 (C=CCO₂R); MS *m/e* (rel. int.): 392.147 (M⁺, 0.5) (C₂₀H₂₄O₈); 374 (M – H₂O, 15); 292 (M – RCO₂H, 6); 83 (C₄H₇CO⁺, 100); 55 (83 – CO, 34); CI (isobutane): M⁺ + 1 393 (44%); 375 (M – H₂O, 33), 245 (375 – CH₂O – RCO₂H, 100).

Agriantholide (6). Impure, colourless gum; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3600 (OH), 1770 (lactone), 1720, 1650 (C=CCO₂R); MS *m/e*

(rel. int.): 358.149 (M – H₂O, 0.3%) (C₂₀H₂₂O₆), 258 (358 – RCO₂H, 2); 83 (C₄H₇CO⁺, 100).

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