the wax to some extent at all stages of growth up to flowering. The occurrence of free *p*-hydroxybenzaldehyde in sorghum epicuticular wax and its relationship to the cyanogenic glucoside dhurrin, also present in high concentration in seedling sorghum is of interest since *p*-hydroxybenzaldehyde is a hydrolysis product of dhurrin, and is discussed by us elsewhere [2].

EXPERIMENTAL

Seeds of *Sorghum bicolor* cv. 65D were obtained from the Botswana Ministry of Agriculture and grown in John Innes No. 2 compost and peat (1:1) in controlled environment rooms. Daylength was 14 hr and temp. was maintained at 30° ± 1° (day) and 25° ± 1° (night). Maximum illumination at plant level from banks of 65/80 W warm white fluorescent tubes was 7500 lx.

Epicuticular waxes were obtained from 7-day-old seedlings (height 10 cm) by immersion of the intact seedlings in distilled Analar chloroform for short periods, extraction being stopped prior to chlorophyll contamination. TLC was done on Si gel G plates (Merck), preactivated at 110° for 30 min, in *n*-hexane–Et_2O–HCO_2H (90:10:0.5). The most polar band (R_f 0.04) was scraped off, eluted with $CHCl_3$ and recrystallized from a mixture of *n*-hexane and $CHCl_3$. Yield was 30% of the total wax, crystals, mp 115°. UV spectrum in neutral solution gave λ_{max} 284 nm (log ϵ 4.20) and in alkaline solution λ_{max} 330 nm (log ϵ 4.44). Mass spectrometry (75 eV) gave *m/z* 122(83), 121(100), 93(41), 65(45), and NMR (in $CDCl_3$) indicates CHO, *s*, 9.90; CH (*ortho* to CHO), *d*, $J = 8$ Hz, 7.81; CH (*ortho* to OH), *d*, $J = 8$ Hz, 6.98; OH, *s*, 1.25.

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EPI-ILICIC ACID FROM *ALCANTARA EKMANIANA**

Ferdinand Bohlmann, Pahup Singh, Harold Robinson† and Robert M. King†

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

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Key Word Index—*Alcantara ekmaniana*; Compositae; Vernonieae; sesquiterpenes; *epi*-ilicic acid.

Abstract—The aerial parts of *Alcantara ekmaniana* afforded, in addition to known compounds, *epi*-ilicic acid. The furanogermacranolides isolated indicate a close relationship between this genus and other members of the same tribe.

The genus *Alcantara* (Compositae, tribe Vernonieae) with one species has been investigated for flavones [1]. We now have studied aerial parts of *A. ekmaniana* (Philipson) H. Robins in more detail. In addition to stigmasterol, lupeol and its Δ-9,11- and Δ-12,13-isomers large amounts of costic (**2**) [2] and isocostic acid (**1**) [3] were isolated. Furthermore, as minor constituents ilicic acid (**4a**) [2], 1-hydroxycostic acid (**3**) [4] and the epimer **5a** of ilicic acid were isolated, which was transformed by addition of diazomethane to the methyl ester **5b** and the pyrazoline **10**. The ^{1}H NMR spectral data (Table 1) of **5b**, if compared with those of **4b**, showed that due to the axial hydroxy group in **5b** H-14 was shifted downfield, while the other signals were similar to those of **4b**. Therefore the only difference between **4b** and **5b** was the stereochemistry at C-4. The more polar parts afforded *p*-hydroxycinnamic acid and the furanoheliangolides **6** [5], **7** [5], **8** [6] and **9** [7], which have all been isolated from genera in the Vernonieae, most of them being placed in the subtribe Lychnophorinae [8] (*Eremanthus*, *Lychnophora*, *Piptolepis*, *Proteopsis*, *Vanillosmopis*). Only *Centratherum*, which may be related to the Lychnophorinae, and one *Vernonia*

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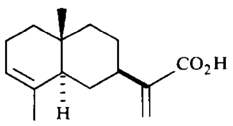
*Part 391 in the series "Naturally Occurring Terpene Derivatives". For Part 390 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21** (in press).



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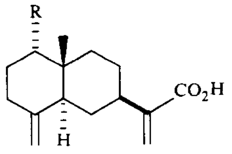

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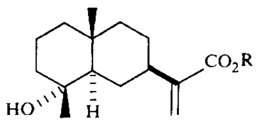
3 R = OH



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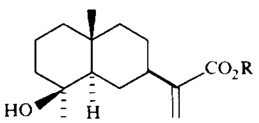
4b R = Me



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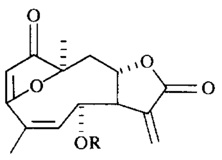
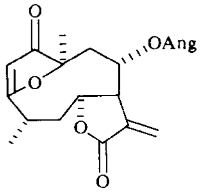


6 R = Ang
7 R = Meacr
8 R = Epang



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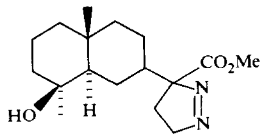

10

species also contain furanoheliangolides. *Alcantara* is only the second member of the subtribe Vernonieae to show this type of lactone. The roots afforded polyisoprene, lupeol and its Δ-9,11- and Δ-12,13-isomers.

EXPERIMENTAL

The air-dried plant material (voucher RMK 8815, deposited in the U.S. National Herbarium, Washington) was extracted with Et_2O–petrol (1 : 2) and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the ^1H NMR spectra with those of authentic material. The aerial parts (600 g) afforded 110 mg stigmasterol, 87 mg lupeol and its Δ-9,11- and 12,13-isomers, 2 mg *p*-hydroxycinnamic acid, 425 mg **1**, 400 mg **2**, 5 mg **3**, 8 mg **4a**, 4 mg **5a**, 90 mg **6**, 2 mg **7**, 34 mg **8**, and 2 mg **9**, while the roots (50 g) gave 1.1 g polyisoprene, 100 mg lupeol and 50 mg of its Δ-9,11- and 12,13-isomers (*ca* 1:1).

Epi-*ilicic acid* (**5a**). Colourless gum, which was purified by addition of CH_2N_2 affording 2 mg **5b** and 1 mg **10**.

5b: Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3615 (OH), 1730 (CO_2R); MS *m/z* (rel. int.): 266.178 $[M]^+$ (12)($C_{16}H_{26}O_3$), 251 $[M-Me]^+$ (53), 248 $[M-H_2O]^+$ (28), 234 $[M-MeOH]^+$ (50), 233 $[281-H_2O]^+$ (58), 206 $[234-CO]^+$ (34), 55 (100).

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Table 1. ^1H NMR spectral data of compounds **4b**, **5b** and **10** (400 MHz, $CDCl_3$, TMS as int. standard)

	4b	5b	10
H-5	1.93 *br d*	1.85 *br d*	1.65 *br d*
H-7	2.53 *dddd*	2.53 *dddd*	1.80 *dddd*
H-13	6.14 *br s*	6.15 *br s*	2.15 *ddd*
H-13′	5.56 *br s*	5.58 *br s*	1.60 *ddd*
H-14	0.92 *s*	1.06 *s*	0.98 *s*
H-15	1.12 *s*	1.15 *s*	1.14 *s*
OMe	3.77 *s*	3.76 *s*	3.78 *s*
H-16	—	—	4.60 *ddd*
H-16′	—	—	4.53 *ddd*

J (Hz): 5α, 6β = 12; 6α, 7α = 4; 6β, 7α = 12; 7α, 8α = 4; 7α, 8β = 12; compound **10**: 13, 13′ = 15; 13, 16 = 5; 13, 16′ = 9; 13′, 16 = 6.5; 13′, 16′ = 9; 16, 16′ = 18.

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