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A DEHYDROFARNESOL DERIVATIVE FROM *STOMANTHES AFRICANUS**

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Key Word Index—*Stomanthes africanus*; Compositae; Eupatorieae; sesquiterpenes; dehydrofarnesol derivative; toxol derivative.

Abstract—*Stomanthes africanus* afforded several *p*-hydroxyacetophenone and dehydronerolidol derivatives. Furthermore, a new dehydrofarnesol was isolated. The chemotaxonomy is discussed briefly.

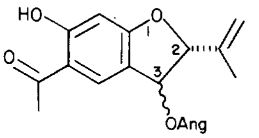
Stomanthes africanus (Oliv. et Hiern.) K. et R. is the only native species of the Eupatoriinae in Africa. So far only one Brazilian species has been investigated chemically[1]. We have now studied the constituents of *S. africanus*, a species in which the occurrence of coumarin has been reported[2]. The roots afforded the tridecapentaynene **1**, germacrene D, euparin (**5**) and the isomeric angelates **3**[3] and **4**. The structure of the latter followed from the ^1H NMR spectrum, which was similar to the spectra of related esters with the same stereochemistry at C-2 and C-3. The aerial parts contained stigmasterol, lupeol, germacrene D, bicyclogermacrene, the tetrayne **2**, the dehydronerolidol derivatives **6**[3] and **7**[4] and the isomeric alcohol **8**. The structure followed from the molecular formula and from the ^1H NMR spectral data of compound **8** and of the corresponding aldehyde **9** obtained by oxidation with manganese dioxide (Table 1). The signals of H-8 through H-13 were similar to those of **7**, indicating identical stereochemistry at C-9 and C-10. The presence of a conjugated triene was deduced from the UV maxima at 278 and 268 nm and the ^1H NMR signals of H-4 through H-6, which were assigned by spin decoupling. The stereochemistry of the 2,3-double bond following from the H-1 and H-2 signals in the ^1H NMR spectrum of the aldehyde **9**, which typically differ from those of an unsaturated aldehyde with the *Z*-configuration.

$Me[C{\equiv}C]_5CH{=}CH_2$

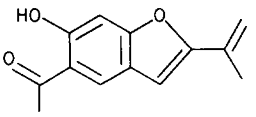
1

$MeCH{=}CH[C{\equiv}C]_4CH{=}CH_2$

2



3 3αH
4 3βH



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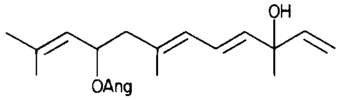

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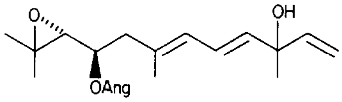

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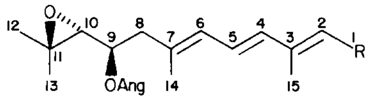

8 R=CH_2OH
9 R=CHO

As *S. africanus* was originally placed in the genus *Eupatorium*, the chemistry supports its placement in a separate genus as nearly all species from *Eupatorium* sens. lat. contain sesquiterpene lactones. The only Brazilian *Stomanthes* species so far investigated also contained *p*-hydroxyacetophenone derivatives similar to compounds **3–5**[1]. These compounds and

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*Part 406 in the series "Naturally Occurring Terpene Derivatives". For Part 405 see Bohlmann, F., Ates (Gören) N. and Grenz, M. (1982) *Phytochemistry* **21**, 1166.

Table 1. ^{1}H NMR spectral data of compounds **8** and **9** (400 MHz, $CDCl_3$, TMS as int. standard)

	8	**9**
H-1	4.29 *br d*	10.13 *d*
H-2	5.15 *br t*	5.94 *d*
H-4	6.15 d	6.25 *d*
H-5	6.42 *dd*	6.94 *dd*
H-6	5.95 *br d*	6.06 *d*
H-8	2.55 *dd* 2.49 *dd*	2.58 *m*
H-9	4.88 *ddd*	4.87 *ddd*
H-10	2.78 *d*	2.79 *d*
H-12	1.37 *s*	1.37 *s*
H-13	1.32 *s*	1.33 *s*
H-14	1.74 *br s*	1.92 *br s*
H-15	1.82 *br s*	2.28 *br s*
OAng	6.02 *qq*	6.06 *br q*
	1.92 *dq*	1.93 *br d*
	1.85 *dq*	1.86 *dq*

J (Hz): 1,2 = 7 (compound **9**: 1,2 = 8); 4,5 = 15.5; 5, 6 = 11; 8, 9 = 4; 8′, 9 = 9; 8,8′ = 14; 9, 10 = 8.

dehydronerolidol derivatives have been isolated from *Eupatorium* [5], *Eupatoriadelphus* (Bohlmann, F., unpublished) and *Austroeupatorium* [6], all members of the subtribe Eupatoriinae [7], which may support the placement of *Stomanthes* in the same subtribe, though these compounds have also been isolated from several other genera of the tribe Eupatorieae. The ability to produce these compounds may therefore be a fundamental one for members of this tribe.

EXPERIMENTAL

The air-dried plant material collected near Pretoria (voucher 81/70, deposited in the Botanical Research Institute, Pretoria) was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated by CC (Si gel) and TLC (Si gel). Known compounds were identified by comparing the ^{1}H NMR spectra with those of authentic material. The roots (150 g) afforded 3 mg germacrene D, 0.1 mg **1**, 8 mg **3**, 10 mg **4** (Et_2O–petrol, 1:1) and 5 mg **5**, while the aerial parts (50 g) gave 50 mg germacrene D, 5 mg bicyclogermacrene, 3 mg stigmasterol, 8 mg lupeol, 0.1 mg **2**, 3 mg **6**, 8 mg **7** and 1.5 and **8** (Et_2O–petrol, 1:1).

6-*Hydroxytoxol angelate* (**4**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1645 (C=O, hydrogen bonded), 1720 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 316.131 $[M]^+$ (6) ($C_{18}H_{20}O_5$), 216 $[M-HO_2CR]^+$ (72), 83 $[C_4H_7CO]^+$ (100); ^{1}H NMR ($CDCl_3$): 6.32 (*d*, H-2), 5.16 (*d*, H-3), 7.88 (*s*, H-4), 6.46 (*s*, H-7), 2.57 (*s*, H-9), 5.28 and 5.10 (*br s*, H-11), 1.82 *br s*, H-12), 13.03 (*s*, OH), 6.10 (*qq*, H-3′), 1.96 (*dq*, H-4′), 1.82 *br s*, H-5′) ($J_{2,3} = 6.5$; $J_{3',4'} = 7$; $J_{3',5} = J_{4',5'} = 1.5$).

9β-*Angeloyloxy*-10α, 11-*epoxydehydrofarnesol* (**8**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720, 1650 ($C{=}CCO_2R$); UV $\lambda_{max}^{Et_2O}$ nm 278, 268; MS *m/z* (rel. int.): 334.214 $[M]^+$ (2) ($C_{20}H_{30}O_4$), 149 $[C_{10}H_{13}O]^+$ (25), 83 $[C_4H_7CO]^+$ (100), 55 $[83-CO]^+$ (78).

1 mg **8** in 2 ml Et_2O was stirred for 1 hr with 20 mg MnO_2. TLC (Et_2O–petrol, 1:3) afforded 0.7 mg **9**, colourless gum, ^{1}H NMR see Table 1.

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