

KOLAVENOL DERIVATIVES FROM *GOYAZIANTHUS TETRASTICHUS**

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Key Word Index—*Goyazianthus tetrastrichus*; Compositae; Eupatorieae; diterpenes; kolavenol derivatives.

Abstract—From the new monotypic genus *Goyazianthus* several kolavenol derivatives were isolated. Their structures were elucidated by spectroscopic methods.

The monotypic Brazilian genus *Goyazianthus* was once part of the genus *Symphyopappus*, but has now been placed in the subtribe Alomiinae [1] on the basis of anatomical characters. We now report on the chemistry of *G. tetrastrichus* (B. L. Robins.) K. et R.

The roots of *G. tetrastrichus* afforded the tricyclic sesquiterpenes 3–5[2, 3], tremetone (6), the angelate 7[4], aesculetin dimethyl ether and the *ent*-kaurene derivatives 8–13, while the aerial parts gave bicyclogermacrene, germacrene D, the hydroxy derivatives 1 and 2, lupeol and its Δ -12, 13-isomer, lupeyl acetate, lupenone, taraxasterol and its acetate, the *ent*-kaurene derivatives 8–14, the flavanoids naringenin and apigenin and five kolavane derivatives. The epoxides 15 and 17, however, could only be separated from each other after acetylation. In addition to 16

and 18, 19 and 20 were also obtained. The ^1H NMR spectral data (Table 1) of 16 and 18 were in part very close to those of an epoxide obtained by boronate reduction of a ketone isolated from a *Hartwrightia* species [5]. Consequently, the stereochemistry at C-2–C-5, C-8 and C-9 was most probably the same. The nature of the side chain followed from the corresponding ^1H NMR signals, which were similar to those of labdanes with the same side chain [6]. The ^1H NMR spectral data of 19 and 20 (Table 1) were only slightly different from those of 16 and 18 respectively. However, the signal of the epoxide proton was replaced by a doublet at δ 5.05, while the mass spectra indicated an additional acetoxy group, which could only be placed at C-3. Most probably, 19 and 20 were formed by ring opening of the epoxide during acetylation. As tertiary alcohols were formed, the stereochemistry at C-4 must be the same as in the epoxides. This required an attack by acetic acid at C-3. The absolute configurations of the diterpenes were not determined.

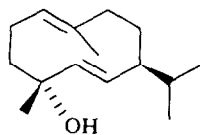
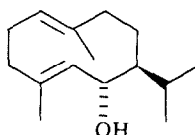
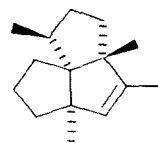
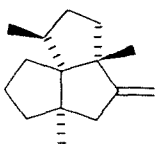
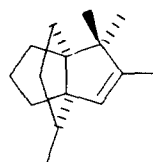
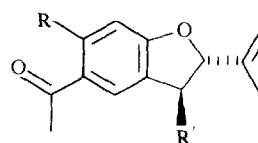
The chemistry of *Goyazianthus* shows some rela-

*Part 398 in the series "Naturally Occurring Terpene Derivatives". For Part 397 see Bohlmann, F., Zdero, C., Robinson, H. and King, R. M. (1982) *Phytochemistry* 21 (in press).

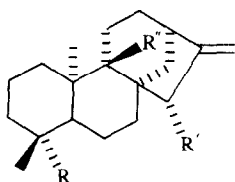
Table 1. ^1H NMR spectral data of compounds 16, 18–20 (400 MHz, CDCl_3 , TMS as int. standard)

	16	18	19	20
H-2	5.04 <i>ddd</i>	5.03 <i>ddd</i>	5.21 <i>ddd</i>	5.21 <i>ddd</i>
H-3	3.12 <i>s(br)</i>	3.08 <i>s(br)</i>	5.05 <i>d</i>	5.05 <i>d</i>
H-14	5.36 <i>t(br)</i>	5.60 <i>t(br)</i>	5.35 <i>t(br)</i>	5.53 <i>t(br)</i>
H-15	4.57 <i>d(br)</i>	4.65 <i>d(br)</i>	4.56 <i>d(br)</i>	4.65 <i>d(br)</i>
H-16	1.73 <i>s(br)</i>	4.62 <i>s(br)</i>	1.71 <i>s(br)</i>	4.63 <i>s(br)</i>
H-17	0.81 <i>d</i>	0.79 <i>d</i>	0.79 <i>d</i>	0.78 <i>d</i>
H-18	1.22 <i>s</i>	1.20 <i>s</i>	1.13 <i>s</i>	1.12 <i>s</i>
H-19	1.08 <i>s</i>	1.07 <i>s</i>	1.06 <i>s</i>	1.05 <i>s</i>
H-20	0.67 <i>s</i>	0.67 <i>s</i>	0.73 <i>s</i>	0.73 <i>s</i>
OAc	2.11 <i>s</i>	2.09 <i>s</i>	2.11 <i>s</i>	2.11 <i>s</i>
	2.06 <i>s</i>	2.06 <i>s</i>	2.05 <i>s</i>	2.05 <i>s</i>
		2.06 <i>s</i>	1.98 <i>s</i>	2.04 <i>s</i>
				1.96 <i>s</i>

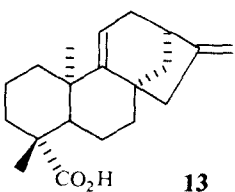
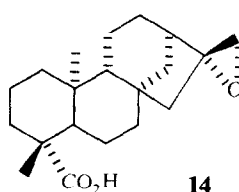
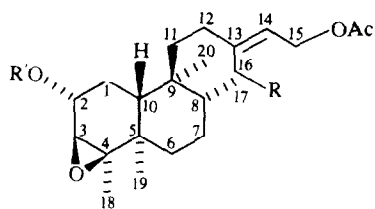
J(Hz): Compounds 16 and 18: 1 α , 2 = 10; 1 β , 2 = 5; 2, 3 = 1.5; 8, 17 = 6; 14, 15 = 7; compounds 19 and 20: 1 α , 2 = 11; 1 β , 2 = 5; 2, 3 = 3.5; 8, 19 = 6; 14, 15 = 7.

**1****2****3****4****5****6****7**

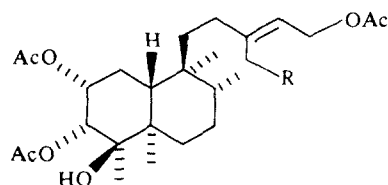
R	H	Me
R'	H	OA _{ng}

**8****9****10****11****12**

R	CO ₂ H	CHO	CH ₂ OH	CO ₂ H	CO ₂ H
R'	H	H	H	OA _{ng}	OA _{ng}
R''	H	H	H	H	OH

**13****14****15****16****17****18**

R	H	H	OH	OA _c
R'	H	Ac	H	Ac

**19** R = H**20** R = OA_c

tionships to that of *Brickellia*, where diterpenes are frequent and from which kolavene derivatives have been isolated [7]. However, more closely related kolavenol derivatives were reported for a *Hartwrightia* species [5]. This genus is placed in the neighbouring subtribe Liatrinae, which also contains sesquiterpene lactones. Kolavene derivatives have been isolated from *Symphyopappus* species [8, 9], but kaurene derivatives, the main constituents of the *Goyazianthus* species, have not so far been reported. The co-occurrence of kolavenol, kaurene and tremetone derivatives as well as the absence of sesquiterpene lactones may be an indication that *Goyazianthus* should remain in the subtribe Alomiinae. However, so far several genera of the Alomiinae have not been studied chemically and more results are necessary before a final conclusion can be reached.

EXPERIMENTAL

Air dried plant material (voucher RMK 8881, deposited in the U.S. National Herbarium, Washington) was extracted with Et₂O-petrol (1:2) and the resulting extracts separated by CC (Si gel) and further by TLC (Si gel). Known compounds were identified by comparing the ¹H NMR spectra with those of authentic material. The roots (120 g) afforded dimethyl ether, 40 mg **8**, 1 mg **9**, 8 mg **10**, 4 mg **11**, 5 mg **12** and 1 mg **13**, while the aerial parts (240 g) gave 46 mg bicyclogermacrene, 47 mg germacrene D, 133 mg lupeol and its Δ-12,13 isomer, 30 mg lupeyl acetate, 3 mg lupenone, 110 mg taraxasterol, 20 mg of its acetate, 40 mg **1**, 12 mg **2**, 20 mg naringenin, 8 mg apigenin, 183 mg **8**, 50 mg **9**, 1.5 mg **10**, 25 mg **11**, 21 mg **12**, 17 mg **13**, 1 mg **14**, 3.5 mg **16** and a mixture of **15** and **17**, which after acetylation afforded 4 mg **18** (Et₂O), 4.5 mg **19** (Et₂O) and 8 mg **20** (Et₂O).

2α,3α-Diacetoxy-4β-hydroxy-3,4-dihydrokolavenol acetate (16). Colourless gum, IR $\nu_{\max}^{\text{CCl}_4}$ cm⁻¹: 1750, 1250 (OAc); MS m/z (rel. int.): 388.261 [M - H₂O]⁺(1) (C₂₄H₃₆O₄), 346.251 [M - HOAc]⁺(14)(C₂₂H₃₄O₃), 286 [346 - HOAc]⁺(18), 205

[C₁₄H₂₁O]⁺(85), 187 [205 - H₂O]⁺(100). [α]_D = +8 (CHCl₃; *c* 0.14).

2α, 16-Diacetoxy-3β, 4β-epoxy-3, 4-dihydrokolavenol acetate (18). Colourless gum, IR $\nu_{\max}^{\text{CCl}_4}$ cm⁻¹: 1750, 1250 (OAc); MS m/z (rel. int.): 404.256 [M - HOAc]⁺(6) (C₂₄H₃₆O₅), 344 [404 - HOAc]⁺(9), 302 [344 - ketene]⁺(21), 205 [C₁₄H₂₁O]⁺(100), 187 [205 - H₂O]⁺(79). [α]_D = +13 (CHCl₃; *c* 0.26).

2α,3α-Diacetoxy-4β-hydroxy-3,4-dihydrokolavevol acetate (19). Colourless gum, IR $\nu_{\max}^{\text{CCl}_4}$ cm⁻¹: 3600 (OH), 1740, 1250 (OAc); MS m/z (rel. int.): 406.272 [M - HOAc]⁺(1)(C₂₆H₄₂O₇), 346[406 - HOAc]⁺(6), 205 (58), 187 (100).

2α, 3α, 16-Triacetoxy-4β-hydroxy-3, 4-dihydrokolavenol acetate (20). Colourless gum, IR $\nu_{\max}^{\text{CCl}_4}$ cm⁻¹: 3500 (OH), 1750 (OAc); MS m/z (rel. int.): 404.256 [M - 2 × HOAc]⁺(6), 344 [404 - HOAc]⁺(7), 284 [344 - HOAc]⁺(15), 205(77) 187 (100).

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REFERENCES

- King, R. M. and Robinson, H. (1977) *Phytologia* **37**, 461.
- Zalkow, L. H., Harris, R. N. III, Van Derveer, D. and Bertrand, J. A. (1977) *J. Chem. Soc. Chem. Commun.* 452.
- Bohlmann, F., LeVan, N., Van Cuong Pham, T., Schuster, A., Zabel, V. and Watson, W. H. (1979) *Phytochemistry* **18**, 1831.
- Bohlmann, F. and Zdero, C. (1971), 964.
- Bohlmann, F., Jakupovic, J., Dhar, A. K., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 843.
- Bohlmann, F., Zdero, C., Dhar, A. K., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 281.
- Bohlmann, F. and Zdero, C. (1976) *Chem. Ber.* **109**, 1436.
- Herz, W., Bhat, S. V., Crawford, H., Wagner, H., Maurer, G. and Farkas, L. (1972) *Phytochemistry* **11**, 372.
- Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, 1657.