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CHEMOTAXONOMY OF THE GENUS *PLEIOTAXIS**

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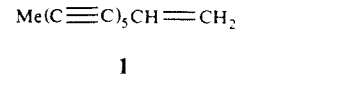
Key Word Index—*Pleiotaxis cf. rugosa*; Compositae; acetylenic compounds; sesquiterpene lactones; chalcones.

Abstract—*Pleiotaxis rugosa* afforded several acetylenic compounds, the sesquiterpenes janerin and the corresponding methacrylate as well as three chalcones, one not being reported previously. The compounds isolated indicate that this genus may be better placed in the Cynareae than in the Mutisieae.

Pleiotaxis (Compositae) is a tropical African genus placed in the tribe Mutisieae. So far nothing is known of its chemistry. We now have investigated *Pleiotaxis cf. rugosa* O. Hoffm. The roots afforded in addition to aplotaxene the acetylenic compounds **1–9** [1], the 2′,4′,6′-trihydroxychalcone derivatives **12** [2] and **13** [3] as well as a further one 2′,6′-dihydroxy-4′-(3,3-dimethylallyloxy)-chalcone (**14**). The latter structure clearly followed from the ^{1}H NMR spectrum. The presence of the *O*-prenyl group could be deduced from the typical signals at δ 4.52, 5.46, 1.79 and 1.73, while the presence of a symmetrical substituted compound followed from the aromatic singlet at δ 5.98 and the *br* singlet at 9.4. The other signals were very similar to those of **12**. The aerial parts also contained **1** and **3–5**. Furthermore, germacrene D, lupeol and its acetate together with their Δ-12,13-isomers as well as janerin (**11**) [3] and 19-desoxy-janerin (**10**) [4] were isolated. The nature of these constituents suggest that this genus may be better placed in the tribe Cynareae, since the acetylenes **3–9** and the guaianolides **10** and **11** are typical for this tribe and have so far never been isolated from representatives of tribe Mutisieae. Further chemical studies of members of the Mutisieae, however, are needed to substantiate this proposal.

*Part 408 in the series "Naturally Occurring Terpene Derivatives". For Part 407 see Bohlmann, F., Borthakur, N., Jakupovic, J. and Pickardt, J. (1982) *Phytochemistry* **21** (in press).



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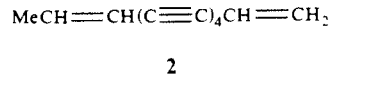

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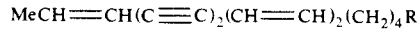
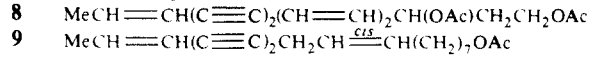


3 R = $CH{=}CH_2$
4 R = CHO
5 R = CH_2CHO
6 R = CH_2CH_2OAc
7 R = CH_2CH_2OH



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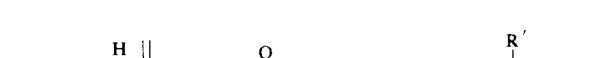

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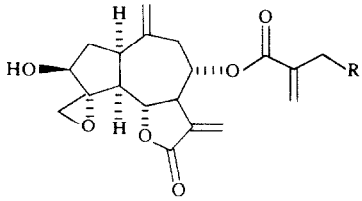
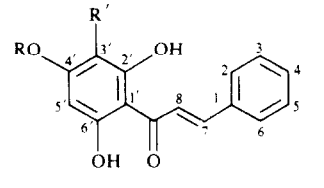


10 R = H
11 R = OH



12 R = H, R′ = $CH_2CH{=}CMe_2$
13 R = Me, R′ = $CH_2CH{=}CMe_2$
14 R = $CH_2CH{=}CMe_2$, R′ = H

EXPERIMENTAL

The air-dried plant material (Botanic Garden, Pretoria, voucher 81/179, deposited in the Herbarium of the Botanic Research Institute, Pretoria) was extracted with Et_2O–petrol, 1:2 and the resulting extracts separated by CC (Si gél) and further by repeated TLC (Si gel). Compounds were identified by comparing the ^1H NMR, UV and MS spectra with those of authentic material. The roots (100 g) afforded 20 mg aplotaxene 1 mg **1**, 3 mg **2**, 5 mg **3**, 1 mg **4**, 1 mg **5**, 8 mg **6**, 2 mg **7**, 7 mg **8**, 2 mg **9**, 5 mg **12**, 4 mg **13** and 2 mg **14**, yellow gum, IR $\nu_{max}^{CCl_4}$, cm^{-1}: 3600–2700, 1630 (hydrogen bonded PhC=O); MS *m/z* (rel. int.): 324.136 $[M]^+$ (22) ($C_{20}H_{20}O_4$), 256 $[M-isoprene]^+$ (64), 255 $[M-CH_2CH{=}CMe_2]^+$ (62), 179 $[256-C_6H_5]^+$ (83), 152 $[255-CH{=}CHPh]^+$ (44), 69 $[Me_2CH{=}CHCH_2]^+$ (100); ^1H NMR ($CDCl_3$, 400 MHz): 7.61 *m* (H-2, H-6), 7.38 *m* (H-3, H-4, H-5), 7.81 *d* (H-7, $J = 16$ Hz), 8.02 *d* (H-8, $J = 16$ Hz), 5.98 *s* (H-3′, H-5′), 4.52 *br s* (H-1″, $J = 7$Hz), 5.46 *tqq* (H-2″, $J = 7, 1, 1$ Hz), 1.79 *br s* (H-4″), 1.73 *br s* (H-5″), 9.40 *br s* (OH). The aerial parts (200 g) gave 10 mg germacrene *D*, 8 mg lupeol, 6 mg of its Δ-12,13-isomer, 10 mg lupeyl acetate, 8 mg of its Δ-12,13-isomer, 0.1 mg **1**, 1 mg **3**, 1 mg **4**, 5 mg **5**, 10 mg **10** and 2 mg **11**

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A BITTER MONOTERPENE GLUCOSIDE FROM *VIBURNUM PHLEBOTRICHUM*

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Key Word Index—*Viburnum phlebotrichum*; Caprifoliaceae; monoterpene glucoside; phlebotricoside.

Abstract—From the methanol extract of the leaves of *Viburnum phlebotrichum*, a new bitter monoterpene glucoside has been isolated in addition to three known compounds, *p*-hydroquinone, arbutin and glucoluteolin. The structures were elucidated by spectroscopic and chemical methods.

INTRODUCTION

The shrub *Viburnum phlebotrichum* is widely distributed in Japan, and its leaves are remarkably bitter. In the course of the investigation on bitter constituents of *Viburnum* species, a new bitter monoterpene glucoside (**1**) was isolated from *V. phlebotrichum* together with three known compounds *p*-hydroquinone, arbutin and glucoluteolin [1]. The bitter glucoside **1**, phlebotricoside, has now been characterized.

RESULTS AND DISCUSSION

The glucoside **1** was obtained upon ether extraction of the methanol extract of fresh leaves and subsequent fractionations by Si gel CC. **1** was optically active and elemental analysis suggested the formula $C_{22}H_{30}O_9$, but no molecular ion corresponding to this was observed in the mass spectrum. The IR spectrum showed strong hydroxyl and aromatic absorptions at 3500 and 1515 cm^{-1}, respectively. In addition, the occurrence of an α,β-unsaturated ester was recognized by the characteristic IR absorptions at 1710 and 1650 cm^{-1} and the absorption at 920 cm^{-1} typical of a terminal methylene group was also observed. The ^1H NMR spectrum of **1** revealed the presence of a *p*-disubstituted phenyl group [δ6.81 and 7.00(4H, A_2B_2, $J = 8$ Hz)], a mono-substituted double bond [5.04–5.28 and 5.91 (3H, ABX system)], a tertiary methyl group attached to a carbon bearing a hydroxyl group [1.30 (3H, *s*)] and an olefinic methyl group [1.80 (3H, *br s*)].

Acetylation of **1** with acetic anhydride–pyridine

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