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MICROGLOSSIC ACID, AN ALICYCLIC DITERPENE AND OTHER CONSITUENTS OF *MICROGLOSSA ZEYLANICA*

A. A. L. GUNATILAKA, B. DHANABALASINGHAM, L. PAREDES,* J. JAKUPOVIC,* F. BOHLMANN* and N. K. B. ADIKARAM†

Department of Chemistry, University of Peradeniya, Sri Lanka; *Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, F.R.G.; †Department of Botany, University of Peradeniya, Sri Lanka

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Key Word Index—*Microglossa zeylanica*; Compositae; alicyclic diterpenes; microglossic acid; dihydromicroglossic acid; dehydrofalcarindiol.

Abstract—The aerial parts of *Microglossa zeylanica* collected in Sri Lanka contained β-farnesene, squalene, dammadienyl acetate, caryophyllen-1,10-epoxide, 5,4'-dihydroxy-6,7,8,3'-tetramethoxyflavone, dehydrofalcarindiol and two new alicyclic diterpenes, microglossic acid and dihydromicroglossic acid. Their structures were elucidated by high field ^{1}H NMR spectroscopy.

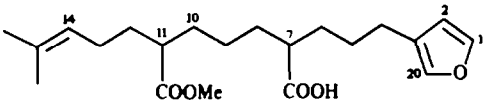
INTRODUCTION

The genus *Microglossa* (Compositae, Astereae) with about 10 species is distributed in Southern and Tropical Africa and South Eastern Asia. So far only the roots of one species from South Africa was studied chemically. As in several other genera of the tribe, dehydrofalcarinone and the corresponding alcohol were isolated [1]. We now have studied the constituents from *M. zeylanica* Benth. et Hook. The aerial parts afforded β-farnesene, squalene, dammadienyl acetate, caryophyllen-1,10-epoxide, 5,4'-dihydroxy-6,7,8,3'-tetramethoxyflavone, dehydrofalcarindiol (**1**) and two new diterpenes, microglossic acid (**3**) and dihydromicroglossic acid (**2**). The structure of **3** followed from the molecular formula $C_{21}H_{30}O_5$ and the ^{1}H NMR spectrum (Table 1) which clearly showed that a β-substituted furan was present. Furthermore the spectrum was in part close to that of centipedic acid [2]. However, one of the olefinic methyl and olefinic proton signals were missing and the chemical shifts of H-10 drastically differed in these two diterpenes. Accordingly, the double bond was *E*-configurated. Spin decoupling showed that the 10,11-double bond was present as H-12 obviously was allylic (δ2.30 *br t*). Further decoupling indicated that the 6,7-double bond was missing and the chemical shift of H-7 (δ2.43 *m*) required a carboxyl group at C-7. As followed from the methoxy singlet at δ3.73, a monoester was present where the conjugated acid was esterified. The ^{1}H NMR data of **2** were close to those of **3** (Table 1). However, the low field signal at δ6.70 was missing. Therefore, in agreement with the molecular formula $C_{21}H_{32}O_5$, the 10,11-dihydro derivative of **3** was present. The configurations at C-7 and C-11 could not be determined.

Similar diterpenes have been isolated from a *Grangea* species [2] which is proposed to be closely related [3]. However, similar furanoditerpenes are also present in *Guitierrezia* [4], *Solidago* [5], *Conyza* [6], *Nardophyllum* [7] and *Plagiochailus* [8] species, all genera of the same tribe. Dehydrofalcarinone and its derivatives have also been reported from several genera of the tribe Astereae.

$H_2C{=}CHCH(OH)[C{\equiv}C]_2CH(OH)(CH_2)_5CH{=}CH_2$

1



2

3 $E\Delta^{10}$

Table 1. ^{1}H NMR spectral data of **2** and **3** (400 MHz, $CDCl_3$, δ-values)

	2	3
H-1	7.33 *t*	7.33 *t*
H-2	6.25 *br s*	6.25 *br s*
H-4	2.43 *br t*	2.43 *br t*
H-5, H-6	1.60 *m*	1.60 *m*
H-7	2.36 *m*	2.43 *m*
H-8	1.60 *m*	1.60 *m*
H-9	1.80 *m*	2.21 *m*
H-10	1.60 *m*	6.70 *t*
H-12	1.60 *m*	2.30 *br t*
H-13	1.94 *br q*	2.07 *br q*
H-14	5.05 *br t*	5.10 *br t*
H-16	1.68 *br s*	1.69 *br s*
H-17	1.59 *br s*	1.59 *br s*
H-20	7.20 *br s*	7.20 *br s*
OMe	3.66 *s*	2.73 *s*

J(Hz): 1,2 = 1,20 = 1.5; 4,5 = 9,10 = 13, 14 = 7.

EXPERIMENTAL

The air dried aerial parts of *M. zeylanica* (400 g, collected in Sri Lanka, voucher No. NKBA 34) was extracted with Et_2O–MeOH–petrol, 1:1:1, and worked-up as reported previously [9]. By CC (SiO_2) and TLC (SiO_2, PF 254) 40 mg β-farnesene, 20 mg squalene, 25 mg dammadienyl acetate, 20 mg caryophyllen-1,10-epoxide, 20 mg **1** and 5 mg 5,4'-dihydroxy-6,7,8,3'-tetramethoxyflavone were obtained and identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material. The polar CC fraction (Et_2O–MeOH, 9:1) gave by HPLC (RP 8, MeOH–H_2O, 7:3, *ca* 100 bar) 2 mg **3** (R_t 3.5 min) and 10 mg **2** (R_t 4.0 min).

10,11-Dihydromicroglossic acid (**2**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500–2700, 1720 (CO_2H), 1740 (CO_2R); MS *m/z* (rel. int.): 364.225, $[M]^+$ (2) (calc. for $C_{21}H_{32}O_5$: 364.225), 346 $[M - H_2O]^+$ (14), 332 $[M - MeOH]^+$ (5), 324 $[346 - MeOH]^+$ (7), 108 (51), 95 (74), 94 (72), 83 (98), 82 (98), 81 (68), 69 (100).

Microglossic acid (**3**). Colourless oil; MS *m/z* (rel. int.): 362.209 $[M]^+$ (6) (calc. for $C_{21}H_{30}O_5$: 362.209), 330 $[M - MeOH]^+$ (5), 284 $[330 - HCO_2H]^+$ (10), 256 $[284 - CO]^+$ (12), 121 (60), 69 (100).

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DITERPENOIDS FROM *VELLOZIA FLAVICANS*

ÂNGELO C. PINTO, DOROTHEA H. T. ZOCHER,* PEDRO P. S. QUEIROZ* and ALPHONSE KELECOM

Instituto de Química, Centro de Tecnologia, Bloco A, Universidade Federal do Rio de Janeiro 21910 Ilha do Fundão, Rio de Janeiro, RJ Brazil; *Núcleo de Pesquisas de Produtos Naturais, Universidade Federal do Rio de Janeiro, CCS, Bloco H, 21941 Cidade Universitária, Rio de Janeiro, RJ. Brazil; Laboratory of Marine Natural Products, Department of General Biology, Universidade Federal Fluminense, C.P. 183, 24000 Niterói, RJ, Brazil

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Key Word Index—*Vellozia flavicans*; Velloziaceae; diterpenes; cleistanthanes.

Abstract—The isolation of three new cleistanthane diterpenes from *Vellozia flavicans* is described and their absolute configurations have been determined by chemical correlation.

INTRODUCTION

In a previous communication, we described the isolation of veadeirol (**1**) and veadeiroic acid (**2**) from the roots, stems and leaf sheaths of *Vellozia flavicans* [1], and we further determined their absolute configurations [2]. We report now the isolation of three new oxygenated cleistanthane diterpenes from the same plant. These have been identified as (4*R*, 5*S*, 10*S*)-cleistantha-8,11,13-trien-19-ol (**3**), (4*R*, 5*S*, 10*S*)-cleistantha-8,11,13-trien-19-oic acid (**4**) and (4*R*, 5*S*, 10*S*)-cleistantha-8,11,13-trien-19-al (**7**).

RESULTS AND DISCUSSION

Fractionation of the hexane extract of *V. flavicans* afforded, in addition to the diterpenes **1** and **2**, an inseparable mixture of alcohols **1** and **3**, and acid **4** invariably contaminated by **2**. Hydrogenolysis of the alcohol mixture yielded unreacted **3** and hydrocarbon **5** which were easily separated by silica gel column chromatography affording pure **3** as a minor constituent (mp 110–112°; $[\alpha]_D + 33°$). Acid **4** could only be purified as its methyl ester derivative **6** (mp 92–95°; $[\alpha]_D + 92°$).