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EPOXYPARVINOLIDE, A SECOCARYOPHYLLANOLIDE FROM *POGOSTEMON PARVIFLORUS**

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Key Word Index—*Pogostemon parviflorus*; Labiatae; secocaryophyllanolide; 4,5-epoxy-9,10-secocaryophyllen-9β,10-olide; friedelin; friedelan-3-ol, phytol.

Abstract—Epoxyparvinolide which belongs to a new class of sesquiterpenoid lactones, the secocaryophyllanolides, was isolated from *Pogostemon parviflorus* along with friedelin, friedelan-3-ol, phytol and sitosterol. Epoxyparvinolide was characterized as 4,5-epoxy-9,10-secocaryophyllen-9β,10-olide.

In continuation of our studies of the genus *Pogostemon* (Labiatae) from Maharashtra [1–3] we report here the isolation and characterization of a new sesquiterpenoid lactone from *Pogostemon parviflorus* along with the other terpenoids phytol, friedelin, friedelan-3-ol and sitosterol which have not been reported previously in this plant.

Parvinolide ($C_{15}H_{22}O_2$) belonging to the caryophyllanolides, a new class of sesquiterpenoid lactones, isolated from the acetone extract of *P. parviflorus* was shown to be caryophyllen-9β,10-olide (**1**) [3] by spectroscopy and X-ray analysis. Further detailed examination of the extract has now yielded a new lactone, epoxyparvinolide of the same class which has been assigned the structure 4,5-epoxy-9,10-secocaryophyllen-9β,10-olide (**2**).

Compound **2**, $C_{15}H_{22}O_3$ ($[M]^+$ at m/z 250); mp 180–182°; $[\alpha]_D$ $+37.59°$ ($CHCl_3$) had two of its three oxygens in a γ-lactone ring ($1775\ cm^{-1}$) and one exomethylene group [$880\ cm^{-1}$; $\delta 5.28$ (1H), 5.46 (1H) and $\delta 143.03$ *s*, 123.50 *t*]. A sharp doublet at $\delta 4.43$ [$\delta 88.78$ *d*] could be assigned to an allylic methine attached to the ethereal oxygen while a double doublet at $\delta 2.92$ was assignable to a methine in a $-\mathrm{O}-\overset{|}{\mathrm{C}}\mathrm{H}-\mathrm{CH}_2-$ group. Comparison of the ^1H NMR spectra of compounds **1** [3] and **2** showed that whereas there were three olefinic protons in **1** there were only two such protons (exocyclic) in **2** and that the signal at $\delta 1.53$ ($\mathrm{Me}-\underset{|}{\mathrm{C}}=\mathrm{CH}-$) in **1** was shifted to $\delta 1.18$ ($\mathrm{Me}-\underset{|}{\overset{\mathrm{O}}{\mathrm{C}}}-\mathrm{CH}-$) in **2**. This reveals that the third oxygen in compound **2** is in the form of an epoxide. The ^{13}C NMR spectrum of compound **2** showed the absence of a trisubstituted double bond in comparison with **1** (absence of signals at $\delta 125.94$ *d*, 134.19 *s* [3]). Compound **2** is therefore 4,5-epoxy-9,10-secocaryophyllen-9β,10-olide.

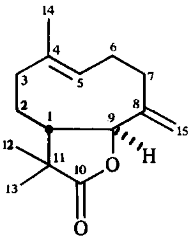
Parvinolide and epoxyparvinolide are the first examples of sesquiterpenoid lactones with the secocaryophyllane skeleton. Therefore, we designate this new lactone skeleton as secocaryophyllanolide. Consequently, parvinolide [3] should be more appropriately described as 9,10-secocaryophyllene-9β,10-olide.

The other compounds isolated from the acetone extract were characterized as a diterpenoid alcohol, *trans*-phytol, two saturated triterpenoids, friedelin and friedelan-3-ol and sitosterol.

EXPERIMENTAL

General experimental details have been described previously [3].

Isolation of terpenoids. The Me_2CO extract (128 g) [3] was chromatographed over silica gel. Elution with C_6H_6 gave fraction A (9.22 g). C_6H_6–Me_2CO (9:1) gave a dark semisolid mass (2.1 g) which was again chromatographed to give friedelin (0.46 g), mp 264–270° (lit. [4] mp 258–259°). IR $\nu_{max}^{nujol}\ cm^{-1}$: 1727 (C=O); friedelan-3-ol (50 mg), mp 290–300°; IR $\nu_{max}^{nujol}\ cm^{-1}$: 3125 (OH); C_6H_6–Me_2CO (9:1) further gave a dark viscous mass (19.9 g) which was rechromatographed over silica gel. Petrol–EtOAc (92:8–90:10) eluted a dark semisolid which on repeated chromatography gave parvinolide (**1**, 0.12 g), mp 134–135° [3] and *trans*-phytol (0.125 g) [5]; IR $\nu_{max}^{neat}\ cm^{-1}$: 3360 (OH); petrol–EtOAc (85:15) eluted sitosterol, mp 138–139°. Petrol–EtOAc (8:2) gave a pasty mass (9 g) which on repeated



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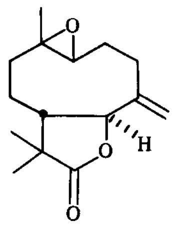

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chromatography gave epoxyparvinolide (**2**) (0.235 g, 0.008 %); mp 180–182° (petrol–C_6H_6); $[\alpha]_D + 37.59°$ ($CHCl_3$, *c* 0.47). (Found: C, 71.70; H, 8.79. Calc. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86 %) IR ν_{max}^{nujol} cm^{-1}: 2940, 1775, 1475, 1390, 1150, 985, 955, 880; ^{1}H NMR: δ1.12 (6H, *s*), 1.18 (3H, *s*), 1.62–2.37 (9H, *m*), 2.92 (1H, *dd*, $J = 2.5$ and 10 Hz), 4.43 (1H, *d*, $J = 10$ Hz), 5.28 (1H), 5.46 (1H). ^{13}C NMR (C-1–C-15 rsp.): δ47.74 (*d*), 21.60 (*t*), 24.21 (*t*), 58.76 (*s*), 64.06 (*d*), 28.55 (*t*), 38.39 (*t*), 143.03 (*s*), 88.78 (*d*), 180.45 (*s*), 43.55 (*s*), 18.07 (*q*)*, 17.34 (*q*)*, 22.75 (*q*)*, 123.50 (*t*) (*assignments may be interchanged). MS *m/z* (rel. int.): 250 $[M]^+$ (6.6), 235 (12), 222 (25), 207 (17.6), 206 (42), 194 (36), 192 (44), 177 (33), 163 (55.5), 152 (50.6), 125 (55.5), 69 (100).

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15-HYDROXY-ACETYLERIOFLORIN AND OTHER CONSTITUENTS FROM *VIGUIERA LINEARIS**

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Key Word Index—*Viguiera linearis*; Compositae; sesquiterpene lactones; diterpene carboxylic acid; 15-hydroxy-acetylerioflorin; heliangolides.

Abstract—Aerial parts of *Viguiera linearis* afforded 16α-hydroxy-*ent*-kauranoic acid, viguiestenin, leptocarpin, acetylleptocarpin, budlein B, clovandiol and the new heliangolide 15-hydroxy-acetylerioflorin.

INTRODUCTION

Several species of the large genus *Viguiera* (tribe Heliantheae, subtribe Helianthineae) have been investigated. Sesquiterpene lactones (germacrolides, heliangolides and furano-heliangolides) [1–8], diterpenes (*ent*-kaurenes [9, 10], modified *ent*-kaurenes [11], *ent*-beyerenes [12–14], *ent*-atisenes [12], *ent*-labdanes [2], and trachylobanes [15]), flavanol compounds [16] as well as cadinadienes [17] have been found as the major constituents of the species belonging to this genus. Here we report the isolation and structure determination of the new heliangolide 15-hydroxy-acetylerioflorin (**2**), and the previously identified compounds 16α-hydroxy-*ent*-kauranoic acid (**1**), viguiestenin (**3**), acetylleptocarpin (**4**), leptocarpin (**5**), budlein B (**6**), and clovandiol (**7**) from a collection of *Viguiera linearis*.

RESULTS AND DISCUSSION

Air-dried and ground leaves and stems of *V. linearis* were extracted with dichloromethane–methanol (1:1). Extensive chromatography of this extract gave seven crystalline substances (**1a**–**7**). The less polar fractions afforded an hydroxy-diterpene carboxylic acid which was identified by its physical constants and methyl ester derivative as 16α-hydroxy-*ent*-kauranoic acid (**1a**) [18, 19]. The previously unreported ^{13}C NMR data agree with the structure and are included in the Experimental.

The new sesquiterpene lactone, 15-hydroxy-acetylerioflorin (**2**), $[\alpha]_D^{25} = -69.4$ (MeOH, *c* 0.167) had molecular formula $C_{21}H_{26}O_8$ (mass spectrometry and elemental analysis) and its IR spectrum showed hydroxyl (3550 cm^{-1}), α-methylene-γ-lactone (1755, 1660 cm^{-1}) and ester (1725 cm^{-1}, broad) absorption bands. The ^{1}H NMR spectrum of **2** exhibited typical signals of an heliangolide with a 3β-OR substitution similar to other heliangolides isolated from this species (*vide infra*). The

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