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# 15-DEOXYGOYAZENSOLIDE, A NEW HELIANGOLIDE FROM *VANILLOSMOPSIS ERYTHROPAPPA**

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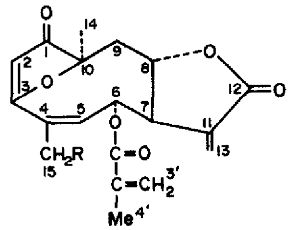
**Key Word Index**—*Vanillosmopsis erythropappa*; Compositae; heliangolide; sesquiterpene lactone.

## INTRODUCTION

In an earlier article [1] the isolation of eremanthin [2] and costunolide from the schistosomicidal wood oil of *Vanillosmopsis erythropappa* Sch. Bip, (Vernonieae, Vernoninae) was reported [3]. We now describe isolation and structure determination of 15-deoxygoyazensolide (**1a**) from a hexane extract of the herbaceous parts of this plant.



**1a** R = H
**b** R = OH

## DISCUSSION

15-Deoxygoyazensolide (**1a**), $C_{19}H_{20}O_6$ (high resolution MS), mp 132–4°, $[\alpha]^{24}_{\mathrm{Hg}}$ −38°, was a γ-lactone with a conjugated exocyclic methylene group (IR band 1770 and 1650 $cm^{-1}$, strong UV end absorption, sharp doublets at 6.21 and 5.45 ppm in the NMR spectrum) and a methacrylic ester function (IR bands at 1710 and 1640 $cm^{-1}$, broad vinyl methyl signal at 1.82 ppm and two multiplets at 6.01 and 5.54 ppm, significant MS peak at *m/e* M–$C_4H_5O$).

The NMR spectrum of the new lactone (see Table 1) was essentially superimposable on that of goyazensolide (**1b**) from *Eremanthus goyazensis* Sch. Bip. [5] except for the resonances of the C-15 hydroxymethylene protons of **1b**, which were replaced by a narrowly-split vinyl methyl triplet at 2.06 allylically coupled to a vinyl proton

Table 1. 270 MHz $^1$H-NMR spectrum of **3a***

| | | | |
|---|---|---|---|
| H-2 | 5·70 | H-13a | 6·21*d* (3·3) |
| H-5 | 6·01*m* | H-13b | 5·45*d* (3·0) |
| H-6 | 5·0*m* (2·0, 2·5) | H-14 | 1·51† |
| H-7 | 3.72*m* (2·5, 2·5, 3·3, 3·0) | H-15 | 2·06*t* (2·0)† |
| H-8 | 4·63*td* (2·5, 11 5) | H-3$^1$a | 6·01*m* (1) |
| H-9a | 2 34*dd* (14,12) | H-3$^1$b | 5·54*m* (1·5) |
| H-9b | 2·29*dd* (2·0, 14·0). | H-4$^1$ | 1·82*m*† |

* Run in $CDCl_3$ with TMS as internal standard. Values are in ppm. Multiplicities are given by the usual symbols. Unmarked signals are singlets. Figures in parentheses are coupling constants in Hz. † Intensity three protons.

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(H-5 at 6.01 ppm) and homoallylically coupled to a proton (H-6) at 5.26 ppm under the carbon carrying the methacrylic ester function. The sequence H-5 through H-9 was established by double resonance as in the case of goyazensolide and will not be discussed in detail. The presence of the dihydrofuran-3-one system C-10 through C-4 required by the formula was supported by the IR (bands at 1700 and 1590 $cm^{-1}$), UV ($\lambda_{max}$266 nm, $\epsilon$ 5600) and NMR spectrum (H-2 singlet at 5.70, methyl singlet at 1.51 ppm). Consequently, the new lactone is **1a** (15-deoxygoyazensolide). The stereochemistry shown in formula **1a** can be assigned on the basis of the same arguments used previously for goyazensolide [5].

## EXPERIMENTAL

*Extraction of* Vanillosmopsis erythropappa. Above-ground parts of the plant (except for the wood), wt 8 kg, collected by Dr. Hermogenes de Freitas Leitão Filho in Campos de Caraguatatuba, vicinity of Caraguatatuba, São Paulo State, Brazil, in May 1971, were extracted with hexane. The crude gum, wt 25 g, was chromatographed over Si gel–$AgNO_3$ (30%), wt 750 g, 200 ml fractions being eluted with hexane containing increasing amounts of EtOAc (hexane), EtOAc acetate and then with EtOAc–EtOH mixtures. The material from fractions 83–92 (hexane–EtOAc 5:1) was combined, wt. 1.29 g; a portion (0.5 g) was further purified by preparative TLC on silica gel (hexane–EtOAc, 2.5:1). The fraction which exhibited a violet fluorescence under UV light was eluted, to yield 45 mg of gum which was recrystallized from hexane to give an amorphous solid, mp 132–4°, $[\alpha]_{Hg}^{24}$ $-38°$ ($CHCl_3$, 7.6 mg/ml), CD curve (MeOH) $[\theta]_{316}$ $+13230$, $[\theta]_{265}$ $-7410$, UV $\lambda_{max}$ 266 nm ($\epsilon$ 5600) and strong end absorption, IR bands at 1770, 1710, 1700, 1650, 1630, and 1590 $cm^{-1}$. The low resolution MS exhibited significant peaks at *m/e* 344 ($M^+$), 275 ($M^+ - C_4H_5O$), 260 ($M^+$–$C_4H_5O$–$CH_3$) and 232 ($M^+$–$C_4H_5O$–Me–CO) (Calc for $C_{19}H_{20}O_6$; C, 66.27; H, 5.85; 0, 27.88; MW, 344.1259. Found C, 65.99; H, 5.74; 0, 27.67; MW(MS), 344.1262).

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# A NEW DITERPENE GALACTOSIDE FROM *ACANTHOSPERMUM HISPIDUM*[*]

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**Key Word Index**—*Acanthospermum hispidum*; Compositae; acanthospermol-$\beta$-galactosidopyranoside; structural determination.

*Plant and origin.* Aerial parts of *Acanthospermum hispidum* DC, Voucher specimen 9/73, JIPMER, collected in Pondicherry, India. The roots of this species contain the widespread tridecapentaynene [1]. The alcoholic extract of fresh aerial parts of *A. hispidum* DC yielded a crystalline compound which on acetylation gives a hexaacetate. The MS leads to the elementary formula $C_{38}H_{56}O_{14}$. The fragments *m/e* 389 and 331 correspond to the compositions $C_{24}H_{37}O_4$ and $C_{14}H_{19}O_9$ respectively and are in agreement with those of a glycoside of a diterpene triol. Acid hydrolysis gives galactose while the diterpene cannot be obtained in an unrearranged form. Also the PMR-spectrum of the hexaacetate is in agreement with an acetylated $\beta$-galactosidopyranoside (Table 1). Furthermore the spectrum shows three Me-singlets, a secondary OCOMe group [*dd* $\delta = 4.75 (J = 2{,}2$ Hz)], the group $CH_2C(Me){=}CH\,CH_2OAc$, a methylene group (*s*(*br*) 4.91 and 5.10) as well as a further secondary $\frown$CHOR group [*dd* 4.43 ($J = 2{,}2$)].These data correspond with a bicyclic diterpene with three O-functions. Manganese dioxide oxidation shows the presence of a primary allylic OH.

Further PMR studies lead to the structure **1**, its absolute configuration not being clear. Also the $^{13}C$ NMR-spectrum is in agreement with **1**. The correlation of the signals could be achieved by an "offresonance"-spectrum and by using $Yb(fod)_3$ as shift-reagent. The observed

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[*] Part 79. in the series "Naturally Occurring Terpene-Derivatives", Part 78. see Bohlmann, F., Zdero C. and Grent M. *Chem. Ber.* (in press).