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A GUAIANOLIDE FROM *GUEVARIA SODIROI**

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Key Word Index—*Guevaria sodiroi*; Compositae; sesquiterpene lactone; guaianolide; guevariolide.

Abstract—A new guaianolide has been isolated from *Guevaria sodiroi*. It has been assigned the trivial name guevariolide and its structure elucidated.

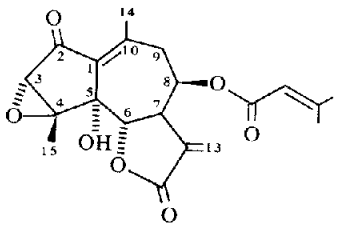
So far no chemical results on *Guevaria* sp. [1] (Compositae, tribe Eupatorieae) are available. This genus is placed in the somewhat arteficial *Piqueria* group [2], which consists of twenty genera. Only representatives of *Ageratum*, *Piqueria* and of the large genus *Stevia*, all placed in the same group, have been investigated up to now. From *Ageratum* species only *p*-hydroxyacetophenone derivatives have been identified [3] while from a *Piqueria* species derivatives of the unusual monoterpene carquejol [4, 5] are reported. The investigations of several *Stevia* species afforded mainly kaurene derivatives [6], a few labdanes [7], bisabolenes [8] and, as very common constituents, longipinene derivatives [8, 9]. However, a few sesquiterpene lactones were also isolated [10, 11].

The aerial parts of *G. sodiroi* (Hieron, in Sod.) K. et R. afforded, in addition to bisabolene, bisabolol, umbelliferone and lupeyl acetate, small amounts of the lactone **1**, which we have named guevariolide. The structure was deduced from the very characteristic ^{1}H NMR data (Table 1). By spin decoupling at 400 MHz in deuteriobenzene all signals could be assigned. Irradiation of the four-fold doublet at δ 3.54 collapsed the typical H-13 doublets and the doublet at 3.86 to singlets, while a broadened double doublet at 5.26 was changed to a doublet. The latter was further coupled with a double doublet at 2.17 and a broadened doublet at 2.57, both showing a geminal coupling. This allowed the assignments of H-6 though H-9. The singlet at 3.10 was obviously due to an epoxide proton, while the methyl singlet at 2.19 must be an olefinic one that was deshielded by a keto group. Only two further signals were present: a broad singlet at 2.16 (1 H) and a sharp singlet at 1.57 (3 H). While the latter obviously had to be placed at the carbon bearing an epoxide, the former was the signal of a hydroxy group as was shown by deuterium exchange. This tertiary hydroxy group must be placed at C-5, as only a guaianolide of type **1** is in agreement with all the data. The stereochemistry at C-8 was deduced from the small coupling $J_{7,8}$, while the α-orientation of the hydroxyl at C-5 followed from the chemical shift of the 6-H signal, which should be more downfield in a lactone with a 5β-hydroxy group. The stereochemistry of the epoxide was

Table 1. ^{1}H NMR spectral data of compound **1** (TMS as internal standard)

	$CDCl_3$	C_6D_6*
H-3	3.56 *s*	3.10 *s*
H-6	4.38 *d*	3.86 *d*
H-7	4.03 *dddd*	3.54 *dddd*
H-8	5.67 *br. dd*	5.26 *br. dd*
H-9	3.24 *br. d*	2.57 *br. d*
H-9′	2.66 *dd*	2.17 *dd*
H-13	6.22 *d*	6.11 *d*
H-13′	5.48 *d*	5.14 *d*
H-14	2.25 *s*	2.19 *s*
H-15	1.79 *s*	1.57 *s*
OCOR	5.33 *qq*	5.59 *qq*
	2.13 *d*	2.08 *d*
	1.89 *d*	1.43 *d*
OH	2.72 *br. s*	2.16 *br. s*

* 400 MHz;
J (Hz): 6, 7 = 10.5; 7, 8 = 2; 7, 13 = 3.5; 7, 13′ = 3; 8, 9 ~ 1; 8, 9′ = 6.5; 3′, 4′ = 3′, 5′ = 1.



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* Part 326 in the series "Naturally Occurring Terpene Derivatives". For Part 325 see Bohlmann, F., Zdero, C., Fiedler, L., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 1141.

deduced from the presence of a hydrogen bond in the IR spectrum. Compound **1** is related to christinin, which has been isolated from a *Stevia* species [11]. This may be an indication of a relationship between the genus *Guevaria* and *Stevia*, though none of the other typical constituents of *Stevia* were isolated. Clearly further investigations are necessary.

EXPERIMENTAL

The air-dried plant material (collected in Ecuador, voucher RMK 7764A) was extracted with Et_2O–petrol (1:2). The resulting extracts were separated first by CC (Si gel) and further by TLC (Si gel). The aerial parts (50 g) afforded 10 mg bisabolene, 6 mg bisabolol, 15 mg lupeyl acetate, 5 mg umbelliferone and about 6 mg **1** (Et_2O–petrol, 1:1).

Guevariolide (**1**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3545 (OH-bonded), 1785 (γ-lactone), 1720, 1625 (C=CC=O), 1720 and 1650 (C=CCO_2R); MS *m/z* (rel. int.): 374.137 (M^+, 7), 274 (M − RCO_2H, 7), 256 (274 − H_2O, 10), 83 ($C_4H_7CO^+$, 100), 55 (83 − CO, 49).

$$[\alpha]_{24°}^{\lambda} = \frac{\begin{matrix}589 & 578 & 546 & 436\,nm\\ -228 & -252 & -286 & -670\end{matrix}}{} (c = 0.15).$$

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