parthenin and tetrahydroparthenin was achieved by using TLC (Si gel) with the solvent system $CHCl_3$–Me_2CO (6:1). Dihydroisoparthenin ($R_f = 0.45$) gave a vivid orange spot with the vanillin reagent fading rapidly on cooling the plate giving a light yellow colour. ^1H NMR (80 MHz, $CDCl_3$ with TMS): δ5.42 (*br s*, H-6), 0.83 (*s*, C-5-Me), 1.12 (*d*, C-10-Me) corresponds to the reported NMR values of dihydroisoparthenin[12].

Identification of hysterin and dihydroisoparthenin in plant samples. Ground shoots (1 g) of samples of *P. hysterophorus* were extracted with 30 ml $CHCl_3$ overnight. Each filtered extract was completely evaporated *in vacuo* and taken for NMR analyses (80 MHz, $CDCl_3$ with TMS). The NMR spectra with the lower field peaks maximized were compared with the characteristic peaks of the NMR spectra of hysterin and dihydroisoparthenin. The crude $CHCl_3$ extracts were chromatographed by two-directional TLC[4] and sesquiterpene lactones identified using the vanillin spray reagent[10].

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DESANGELOYLSHAIRIDIN, A SESQUITERPENE LACTONE FROM *GUILLONEA SCABRA*

MARIANO PINAR, MANUEL RICO and BENJAMÍN RODRÍGUEZ

Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, Madrid-6, and Instituto de Estructura de la Materia, CSIC; Serrano 119, Madrid-6, Spain

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Key Word Index—*Guillonea scabra*; Umbelliferae; new guaianolide; desangeloylshairidin.

Abstract—From the roots of *Guillonea scabra* a new sesquiterpene lactone has been isolated. Its structure has been established by spectroscopic means as desangeloylshairidin.

INTRODUCTION

In a previous communication [1] we reported guaiol, malaphilinin [2] and badkysin (**1**) [3] as the sesquiterpene constituents of the roots of *Guillonea scabra* (Cav.) Cosson (= *Laserpitium scabrum* Cav.). New study of the plant material and careful chromatography of the fractions containing badkysin (**1**), has now allowed the isolation of two other sesquiter-

Table 1. Chemical shifts* (δ, ppm from TMS) and coupling constants (Hz) of compounds **2** and **3**

	2†	3
H-3	6.27 *q*, $\|J_{3,15}\| = 1.2$	6.22 *q*, $\|J_{3,15}\| = 0.9$
H-5	3.15 *d*, $J_{5,6} = 10.5$	3.07 *dq*, $J_{5,6} = 11$, $\|J_{5,15}\| = 0.6$
H-6	4.58 *dq*, $J_{6,5} = 10.5$, $\|J_{6,13}\| = 1.9$	4.73 *dq*, $J_{6,5} = 11$, $\|J_{6,13}\| = 1.8$
H-8	6.22, partially overlapped	5.10 *dd*, $J_{8\alpha,9\alpha} = 1.5$, $J_{8\alpha,9\beta} = 5.7$
H-9α	2.68 *dd*, $J_{9\alpha,8\alpha} = 1.4$, $J_{9\alpha,9\beta} = -14.3$	2.58 *dd*, $J_{9\alpha,8\alpha} = 1.5$, $J_{9\alpha,9\beta} = -13.5$
H-9β	2.85 *dd*, $J_{9\beta,8\alpha} = 6.4$, $J_{9\beta,9\alpha} = -14.3$	2.72 *dd*, $J_{9\beta,8\alpha} = 5.7$, $J_{9\beta,9\alpha} = -13.5$
13-Me	2.06 *d*, $\|J_{13,6}\| = 1.9$	1.92 *d*, $\|J_{13,6}\| = 1.8$
14-Me	2.47 *s*	2.48 *s*
15-Me	2.38 *d*, $\|J_{15,3}\| = 1.2$	2.35 *dd*, $\|J_{15,3}\| = 0.9$, $\|J_{15,5}\| = 0.6$

*All these assignments have been confirmed by double resonance experiments.

†Angeloyl group: 6.18 (1H, $J_{vic} = 7.0$, $J_{allylic} = 2.0$), 1.93 (3H, $J_{vic} = 7.0$, $J_{homoallylic} = 1.8$) and 1.84 (3H, $J_{allylic} = 2.0$, $J_{homoallylic} = 1.8$).

penes: the recently described shairidin (**2**) [4], and its desangeloyl derivative (**3**), which is a new natural compound.

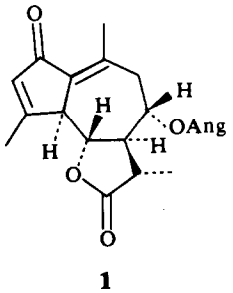
As, in our opinion, the structure **2** assigned to shairidin requires a more detailed justification than the one given by the Soviet authors [4], we report here further evidence on structure **2**, which is also confirmed by the ^{1}H NMR data of the new desangeloyl derivative, **3**.

RESULTS AND DISCUSSION

The structure **2** for shairidin [4] can be completely confirmed from its ^{1}H MMR spectrum (Table 1), taking into account the data of the closely related structure, badkysin (**1**) [3]. The doublet (3H, J = 7.5 Hz) at δ 1.35 in the ^{1}H NMR spectrum of the latter compound (**1**) has been changed for a doublet (3H, J = 1.9 Hz) at δ 2.06 in the spectrum of **2**, which showed almost identical signals that badkysin for the angeloyl group, for the cyclopentenone moiety and for the C-14 and C-15 methyl groups. All these facts point toward structure **2** for shairidin, because the above data agree with the introduction of a double bond between C-7 and C-11 carbon atoms of the lactone ring of badkysin. The presence of an α,β-unsaturated lactone ring in **2** is also revealed by comparing its IR and UV spectra with those of badkysin (**1**): ν_{CO}^{Nujol} (cm^{-1}): 1767 in **1**, 1754 in **2**; λ_{max}^{EtOH} 230 nm (log ϵ 4.29) in substance **2** (see also Experimental).

In the ^{1}H NMR spectrum of shairidin (**2**), the H-8 signal overlaps with those of the olefinic protons, but analysis of the two-proton signal (H-9α and H-9β) in the δ 2.6–2.9 region as the AB part of an ABX system yields the following values: δ_A 2.85, δ_B 2.68, $J_{AB} = -14.3$ Hz, $J_{AX} = 6.4$ and $J_{BX} = 1.4$ Hz. The values obtained for the vicinal coupling between H-8 and C-9 methylene group, when compared with those obtained for badkysin (**1**) [3] ($J_{8\beta,9\alpha} = 9.6$, $J_{8\beta,9\beta} = 4.5$ Hz), suggest a change in the configuration of the C-8 center in **2** with respect to badkysin (**1**). No proton–proton *trans*-diaxial arrangement seems to exist in the C-8–C-9 fragment, since no vicinal coupling larger than 9 Hz has been observed for **2**. The vicinal couplings of 6.4 and 1.4 Hz are accommodated more properly by assuming that the angeloyloxy group is a β-substituent, thus having H-8α in an equatorial (or pseudo-equatorial) configuration.

On the other hand, the ^{1}H NMR spectrum of **3** (Table 1) is identical with that of shairidin (**2**), but lacking the signals due to the angeloyl moiety and showing the signal of the H-8 proton diamagnetically shifted (δ 5.10). The coupling constants of this proton with the vicinal C-9 methylene group are $J_{8\alpha,9\alpha} = 1.5$ and $J_{8\alpha,9\beta} = 5.7$ Hz, in agreement with the previous conclusions on the stereochemistry of the C-8 center. Thus, the proposed structure, **2**, for shairidin [4] is confirmed and the structure of the new natural guaianolide, **3**, as its desangeloyl derivative is established.



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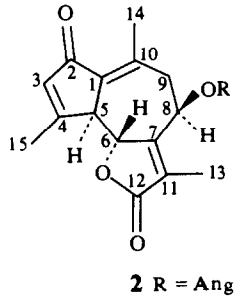

2 R = Ang
3 R = H

EXPERIMENTAL

For general experimental details, see ref. [1].

Isolation of shairidin (**2**). The chromatographic fractions containing impure badkysin (**1**, 630 mg) were carefully and repeatedly chromatographed over Si gel plates with $CHCl_3$ as eluent. Pure shairidin (**2**, 150 mg) (less polar component) was isolated: mp 145–146° (from Et_2O); $[\alpha]_D^{23}$ +21° (*c* 0.72; $CHCl_3$); IR ν_{max}^{Nujol} cm^{-1}: 1754 (lactone), 1690, 1650, 1620, 1265, 1140, 1023, 765; UV λ_{max}^{EtOH} nm (log ϵ): 255 (4.23), 230 (4.29) (α,β-unsaturated lactone). ^{1}H NMR (90 MHz, $CDCl_3$): see Table 1. EIMS (direct inlet) 75 eV, *m/z* (rel. int.): 342 (M^+, 23), 243 (31), 242 (46), 227 (9), 214 (9), 199 (23), 186 (17), 96 (14), 91 (17), 83 (100), 55 (83). (Found: C, 70.44; H, 6.47. Calcd. for $C_{20}H_{22}O_5$: C, 70.16; H, 6.48%.)

Isolation of **3**. The chromatographic fraction (2 g) obtained after elution of scoparone [1] was chromato-

graphed over Si gel plates eluted with $CHCl_3$ as eluent. After repeated crystallization from MeOH, **3** (100 mg) was obtained, mp 226–229°; $[\alpha]_D^{23}$ +41° (*c* 0.86; $CHCl_3$); IR ν_{max}^{KBr} cm^{-1}: 3300 (hydroxyl), 1750 (γ-lactone), 1675 (cyclopentenone), 1632, 1618 (olefinic bonds), 1418, 1390, 1325, 1290, 1231, 1205, 1100, 1085, 1045, 1010, 865, 765, 684. UV λ_{max}^{EtOH} nm (log ϵ): 257 (4.18) (cyclopentenone chromophore), 235 (4.02) (α,β-unsaturated lactone). ^1H NMR (90 MHz, $CDCl_3$): see Table 1. EIMS (direct inlet) 75 eV, *m/z* (rel. int.): 260 (M^+, 100), 245 (6), 242 (13), 227 (8), 214 (8), 199 (23), 197 (19), 186 (14), 185 (13), 171 (14), 143 (11), 135 (66), 126 (60), 107 (40), 105 (16), 98 (16), 91 (65), 77 (28), 69 (81), 65 (30), 51 (30), 44 (39). (Found: C, 68.94; H, 6.30. $C_{15}H_{16}O_4$ requires: C, 69.21; H, 6.20%.)

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ISOLATION AND STRUCTURE OF STEPHALIC ACID, A NEW CLERODANE DITERPENE FROM *STEVIA POLYCEPHALA**

ENRIQUE ANGELES, KIRSTEN FOLTING,† PAUL A. GRIECO,† JOHN C. HUFFMAN,† R. MIRANDA and MANUEL SALMÓN‡

Escuela Nacional de Estudios Profesionales Cuautitlan, UNAM Cuautitlan Izcalli, Campo 1, Departamento de Química, Estado de México, México; †Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405, U.S.A.; ‡Instituto de Quimica, Universidad Nacional Autónoma de México, México 20, D. F., México.

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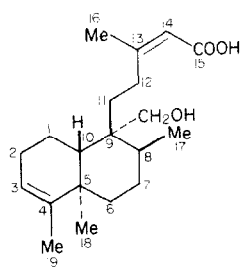
Key Word Index—*Stevia polycephala*; Compositae; stephalic acid; clerodane derivatives; diterpenes.

Abstract—From the methanolic extract of *Stevia polycephala* a new clerodane-type diterpene, stephalic acid, was isolated. The structure and stereochemistry were determined by a combination of spectral data and single-crystal X-ray analysis.

The *Stevia* genus is one of the largest found in Mexico [1]. Sesquiterpene lactones [2–4] and diterpenes [5] have been isolated from the non-polar or chloroform fractions of Mexican *Stevia* species. Isohumelene and new α-longipinene derivatives have been isolated from *Stevia polycephala* [6]. In our continuing search for new natural products from *Stevia* species, we examined the polar fraction of the methanolic extract of *S. polycephala* collected in the state of Tlaxcala, Mexico, and have isolated a new diterpene, stephalic acid (**1**), which possesses the clerodane carbon skeleton.



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Fractionation of the methanol extract of *S. polycephala* with ethyl acetate and chromatographic separation employing Si gel provided a new diter-

*Contribution No. 563.