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# DESANGELOYLSHAIRIDIN, X-RAY STRUCTURE DETERMINATION OF A SESQUITERPENE LACTONE FROM *GUILLONEA SCABRA*

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**Key Word Index**—*Guillonea scabra*; Umbelliferae; guaianolide; desangeloylshairidin; absolute configuration; conformational analysis.

**Abstract**—The structure and absolute configuration of desangeloylshairidin, a guaianolide isolated from *Guillonea scabra*, have been established by X-ray diffraction analysis. No conformational change was observed in its seven-membered ring between the crystal and deuterochloroform solution states.

## INTRODUCTION

In previous communications [1, 2] we reported the isolation of two new sesquiterpene constituents of the roots of *Guillonea scabra* Cav. Cosson., an umbelliferous plant endemic in the Iberian Peninsula. These were desangeloylshairidin (**1**) and guillonein (**2**). Recently, the structure and absolute configuration of the latter was rigorously established by X-ray analysis [2]. The observation [2] that guillonein (**2**), in going from the crystal to deuterochloroform solution, undergoes a conformational change in its seven-membered ring, left open an alternative to the proposed structure of desangeloylshairidin (**1**). This prompted us to obtain the X-ray diffraction crystalline molecular structure of **1** to definitely establish its structure and absolute configuration, which is reported in this paper.

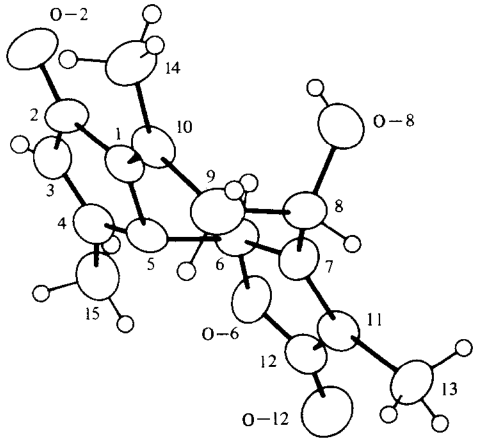
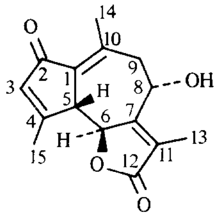
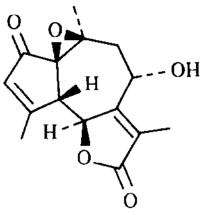


Fig. 1. Absolute X-ray molecular model of desangeloylshairidin (**1**).



**1**



**2**

## RESULTS AND DISCUSSION

Figure 1 shows the X-ray absolute molecular model of desangeloylshairidin (**1**). The seven-membered ring has a chair conformation, with C-7 at 0.55 Å out of the plane C-5–C-6–C-8–C-9 and C-1=C-10 at 1.06 Å. This configuration and conformation are the same as that found in guillonein (**2**) [2]. The Cremer [3] parameters of this ring in **1** and **2** are: $\theta_2 = 38°$, $\Phi_2 = 51°$, $\Phi_3 = 79°$, $QT = 0.60$ Å and $\theta_2 = 35°$, $\Phi_2 = 56°$, $\Phi_3 = 79°$, $QT = 0.77$ Å, respectively. This calculation starts at C-1 in the sense of C-1 → C-5. The double bond C-1=C-10 of 1.345 (6) Å in desangeloylshairidin (**1**) increases the planarity around, making the group C-1–C-2–C-3–C-4–C-5–C-9–C-10–C-14–C-15–O-2 planar. The crystal structure of **1** is built by one intermolecular hydrogen bond between O-8–H .... O-2 with O-8 .... O-2 = 2.745 (6) Å and the angle at the hydrogen atom is 172°.

Comparison of the X-ray analyses of **1** and **2** shows a complete analogy between their intermolecular structures. As discussed in a previous work [2], the ${}^3J_{8,9}$ and ${}^3J_{8,9'}$ coupling values, obtained from the ${}^1$H NMR spectrum of compound **2** in deuterochloroform solution, were not compatible with the corresponding torsion angles observed in the crystal, so that we concluded that a conformational change of the seven-membered ring from the chair C(7) to the twist-hinge TH′(7) form takes place in going from crystal to solution. This observation and the observed ${}^3J_{8,9} = 6.3$ Hz and ${}^3J_{8,9'} = 1.0$ Hz values of desangeloylshairidin (**1**), opened the possibility of two alternatives for the structure of this compound in deuterochloroform solution: (a) a C(7) conformation for the seven-membered ring with an $\alpha$-configuration for the C-8 hydroxyl substituent; or (b) a TH′(7) conformation with a $\beta$-configuration for the hydroxyl grouping. The results obtained in this work definitely show that the first alternative prevails, as was put forward earlier [1, 2] on the basis of characteristic esterification shifts. It is noteworthy that, in contrast to guillonein (**2**) [2], desangeloylshairidin (**1**) maintains in deuterochloroform solution the seven-membered ring conformation shown in the crystalline state.

## EXPERIMENTAL

For the isolation of desangeloylshairidin from *Guillonea scabra*, see ref. [1].

*X-ray structure determination of* **1**. Crystals of $C_{15}H_{16}O_4$ are monoclinic, space group $P2_1$, with unit cell parameters $a = 10.7632(6)$, $b = 6.7807(3)$, $c = 9.1438(5)$ Å, $\beta = 106.219(2)^\circ$, $Z = 2$ and $D_c = 1.349$ g/cm$^3$.

The data were collected on a four circle diffractometer with graphite-monochromated Cu$K\alpha$ radiation. The intensities of 1184 independent Friedel pairs up to $\theta = 65^\circ$ were measured in the $\omega/2\theta$ scan mode with a scan rate of 0.025°/sec. No absorption correction was done ($\mu = 7.63$ cm$^{-1}$), and no crystal decomposition was observed throughout the expt. The structure was solved by MULTAN [4] and refined using the 1020 observed reflexions with $I > 2\sigma(I)$. All H atoms were verified on a difference map and were included in the refinement as fixed isotropic contributors. A convenient weighting scheme was used to have no dependence of $\langle w\Delta^2 F \rangle$ vs. $\langle F_0 \rangle$ and $\langle \sin\theta/\lambda \rangle$. The last cycles of weighted refinement, including both $hkl$ and $hkl$ reflexions, gave $R = 0.047$ and $R_w = 0.060$ [5].

The absolute configuration was determined comparing the 44 more relevant Bijvoet pairs with $F_0 > 10\sigma\,(F_0)$, $\Delta F_c > 0.04$, $2.5 < F_0 < 10$ and $0.37 < \sin\theta/\lambda < 0.60$, which include data with minimum exptal error. The averaged Bijvoet difference was 0.177 for the right enantiomer vs. 0.199 for the wrong one*.

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## REFERENCES

1. Pinar, M., Rico, M. and Rodríguez, B. (1982) *Phytochemistry* **21**, 1802.
2. Pinar, M., Rodríguez, B., Rico, M., Perales, A. and Fayos, J. (1983) *Phytochemistry* **22**, 987.
3. Cremer, D. and Pople, J. A. (1975) *J. Am. Chem. Soc.* **97**, 1354.
4. Main, P. (1980) MULTAN-80, Department of Physics, University of York, U.K.
5. Stewart, J. M., Kundell, F. A. and Baldwin, J. C. (1970) *The X-Ray 70 System*, Computer Science Center, University of Maryland, College Park, U.S.A.

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*A list of atomic, positional and thermal parameters, bond distances and angles, torsional angles, conformational parameters and $F_0$–$F_c$ tables are deposited at the Cambridge Crystallographic Data Centre.