Phytochemistry, Vol. 22, No. 2, pp. 599–600, 1983.
Printed in Great Britain.

0031–9422/83/020599–02$03.00/0

PSEUDOGUAIANOLIDES FROM *GAILLARDIA ARISTATA*

STANISŁAW GILL, WANDA DEMBIŃSKA-MIGAS, MARIA ZIELIŃSKA-STASIEK, WŁODZIMIERZ MARIA DANIEWSKI* and ANDRZEJ WAWRZUŃ*

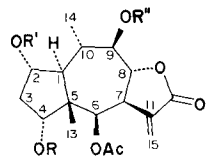
Department of Pharmacognosy, Institute of Technology and Drug Analysis of Medical Academy, Gdańsk, Poland; *Institute of Organic Chemistry, Polish Academy of Sciences, 00–961 Warsaw, M. Kasprzaka 44, Poland

(*Revised received* 12 *July* 1982)

Key Word Index—*Gaillardia aristata*; Compositae; pseudoguaianolide spathulin derivatives.

Abstract—The aerial parts of *Gaillardia aristata* afforded a new pseudoguaianolide, 9-*O*-desacetylspathulin-2-*O*-2-methylbutanoate.

The aerial parts of *Gaillardia aristata* of North American origin have been investigated previously. From the collection made in Colorado the pseudoguaianolide spathulin (**1**) was isolated and its structure determined [1, 2]. Compound **1** was also found in many other species of the subtribe Gaillardinae and its structure was confirmed by X-ray analysis [3]. Plant material collected in Alberta, Canada, afforded, in addition to **1**, a eudesmanolide 3-epi-isotelekin [4]. Other eudesmanolides, pulchelin C and pulchelin E, were isolated from the collection obtained in Albany County, Wyoming [voucher specimen No. ROA-71-17 (RM)] [5]. A reinvestigation of this species cultivated in Poland afforded a crystalline product which



	1	2	3	4
R	H	H	H	Ac
R'	H	2-MeBu	Ang	2-MeBu
R"	Ac	H	H	Ac

seemed to be pure as judged by TLC in several solvents. However, its ^{1}H NMR spectrum showed it to be a mixture of two different esters. Therefore, the mixture was subjected to HPLC and two pseudoguaianolides, **2** and **3** (order of elution) were obtained. Compound **3** was identified as 9-*O*-desacetylspathulin-2-*O*-angelate. Its physical properties and spectral data were identical with those published previously [6]. Careful examination of the ^{1}H NMR spectrum of **2** showed that this was the 2-methylbutanoate. The chemical shifts of the sesquiterpene protons, as well as their multiplicity, were identical with those of the ^{1}H NMR spectrum of **3** (Table 1), the only difference being in the signals of the protons of the ester groups. Acetylation of **2** gave spathulin-4-*O*-acetate-2-*O*-2-methylbutanoate [2] whose ^{1}H NMR spectrum exhibited the signals of the H-4β and H-9α protons shifted downfield compared with those in the spectrum of **2** (Table 1). All these facts unambiguously proved the structure of **2** as 9-*O*-desacetylspathulin-2-*O*-2-methylbutanoate, which could be formed in the plant by selective reduction of **3**.

Table 1. ^{1}H NMR spectral data of compounds **2**, (220 MHz, $CDCl_3$, TMS as int. standard) and **4** (100 MHz, $CDCl_3$, TMS as int. standard)

	2	4
H-1α	2.32 *dd*	—
H-2β	4.95 *m*	5.01 *m*
H-3α	2.64 *ddd*	2.60 *m*
H-3β	1.67 *dd*	1.60 *dd*
H-4β	3.79 *d*	4.81 *d*
H-6α	5.97 *d*	5.78 *d*
H-7α	3.18 *m*	3.28 *m*
H-8β	4.52 *dd*	4.60 *dd*
H-9α	3.37 *br t*	4.90 *m*
H-10β	1.89 *m*	1.9 *m*
H-13	6.28 *d*	6.27 *d*
H-13'	5.45 *d*	5.49 *d*
H-14	1.21 *d*	0.93 *d*
H-15	0.80 *s*	0.89 *s*
OAc	2.04 *s*	2.00 *s*
		2.12 *s*
		2.14 *s*
OCOR	2.37 *m*	
	1.72 *m*	
	1.48 *m*	
	1.13 *d*	1.13 *d*
	0.91 *t*	0.95 *t*

J (Hz): 1α, 2β = 7.5; 1α, 10β = 11.5; 2β, 3α = 9; 2β,3β = 2; 3α,3β = 16.5; 3α,4β = 4.5; 6α,7α = 3.5; 7α,8β = 9; 7α, 13 = 3.5; 7α, 13' = 3.2; 8β,9α = 10; 9α,10β = 10; 10β, 14 = 7; OMeBu; 2',3' = 3',4' = 2',5' = 7; 3'$_1$,3'$_2$ = 12.

EXPERIMENTAL

Gaillardia aristata Pursh was grown in Gdańsk Medical Academy Botanical Garden from seeds obtained from the University of Warsaw Botanical Garden (Index Seminum 1971, Hortus Botanicus Universitatis Varsoviensis No. 739).

The purified $CHCl_3$ extract (56 g) obtained [1] from the dried plant (3 kg) was subjected to CC on Si gel (800 g) which was eluted first with pure C_6H_6 and subsequently with C_6H_6–$CHCl_3$ mixtures (8:2, 6:4, 1:1, 3:7). Fractions eluted with C_6H_6–$CHCl_3$ (8:2 and 6:4) were combined and evaporated. The residue was purified by CC on Si gel (100 g) eluted with $CHCl_3$–Et_2O (7:3) and recrystallized from MeOH–Me_2CO

(9:1) to gave a mixture of **2** and **3** (1.95 g) (plates mp 199–201°). Esters **2** and **3** were separated by HPLC using a series of five 9 mm × 30 cm columns packed with Lichrosorb 10. The columns were eluted with EtOAc–hexane (3:7), flow rate 5 ml/min. To obtain a complete preparative separation the solute (40 mg) had to be recycled × 4. A RI detector was used for monitoring the chromatography. 9-*O*-Desacetylspathulin-2-*O*-2-methylbutanoate (**2**, 8 mg) had mp 198°; $[\alpha]_D^{20}$ + 24° (*c* 0.5); IR ν_{max} cm^{-1}: OH 3600, C = O lactone 1765, C = O ester 1720. MS *m/z* (rel. int.): 424.2 $[M]^+$ (0.05), 362.2 (27), 322 $[M - RCO_2H]^+$ (28), 262 $[322 - HOAc]^+$ (100). (Found: C, 62.15; H, 7.50. $C_{22}H_{32}O_8$ requires: C, 62.25; H, 7.60%.) 9-*O*-Desacetylspathulin-2-*O*-angelate (**3**, 28 mg) had mp 226°; $[\alpha]_D^{20}$ + 39.0° (*c* 0.9).

Acetylation. Compound **2** (16 mg) was dissolved in a mixture of pyridine (5 ml) and Ac_2O (2 ml) and left overnight. Standard work-up of the reaction mixture gave **4** (18.2 mg), 95% as colourless needles, mp 86–88°. $[\alpha]_D^{20}$ − 0.2° (*c* 0.9); IR ν_{max} cm^{-1}; no OH, C = O lactone 1765, C = O ester 1730; MS *m/z* (rel. int.): 508 $[M]^+$ (3); 406 $[M - HOCOR]^+$ (8); 346 $[406 - HOAc]^+$ (11); 286 $[346 - HOAc]^+$ (11); 85 $[C_4H_9CO]^+$ (100); 43 $[MeCO]^+$ (12). (Found: C, 61.1; H, 7.06. $C_{26}H_{36}O_{10}$ requires: C, 61.40; H, 7.13%.)

REFERENCES

1. Herz, W., Rajappa, S., Lakshmikantham, M. V., Raulais, D. and Schmid, J. J. (1967) *J. Org. Chem.* **32**, 1042.
2. Herz, W. and Srinivasan, A. (1974) *Phytochemistry* **13**, 1171.
3. Inayama, S., Ohkura, T. and Itaka, Y. (1977) *Chem. Pharm. Bull. Jpn.* **25**, 1928.
4. Herz, W., Subramanian, P. S. and Geissman, T. A. (1968) *J. Org. Chem.* **33**, 3743.
5. Mitchell, D. R. and Asplund, R. O. (1973) *Phytochemistry* **12**, 2541.
6. Gill, S., Dembińska-Migas, W., Śliwińska, E., Daniewski, W. M. and Bohlmann, F. (1980) *Phytochemistry* **19**, 2049.

Phytochemistry, Vol. 22, No. 2, pp. 600–601, 1983.
Printed in Great Britain.

0031-9422/83/020600-02$03.00/0
Pergamon Press Ltd.

UCRIOL, AN EPOXY-DITERPENE FROM *SIDERITIS SYRIACA*

PIETRO VENTURELLA, AURORA BELLINO and MARIA LUISA MARINO

Institute of Organic Chemistry, University of Palermo 20, via Archirafi, 90123 Palermo, Italy

(*Received* 14 *June* 1982)

Key Word Index—*Sideritis syriaca* (*S. sicula* Ucria); Labiatae; epoxy-diterpene; ent-15β,16β-epoxykaurane-7β,18-diol.

Abstract—The isolation of a new epoxy-diterpene from the inflorescence of *Sideritis syriaca* (*S. sicula* Ucria) is described. Its structure and stereochemistry were established by spectroscopy and partial synthesis.

INTRODUCTION

From the aerial part, and mainly from the corollas and inflorescence of *Sideritis syriaca* L. (*S. sicula* Ucria) [1] we have extracted eight new diterpenoids of the ent-kaurene–isokaurene [2] type. A new study of the petrol extract of the inflorescence of this plant has now allowed the isolation of another diterpenoidic substance for which we propose the name 'ucriol' and the structure **1** on the basis of chemical and spectroscopic results.

RESULTS AND DISCUSSION

A careful chromatographic investigation of the mother liquors from the isolation of the major diterpenic constituents indicated the presence of a very small amount of a new diterpene. Ucriol (**1**), mp 185–186°, $C_{20}H_{32}O_3$, (analytical and mass spectra, *m/z* 320 $[M]^+$) gives a negative TNM and has no UV spectrum. The IR spectrum shows hydroxyl absorption and no band for a carbonyl group. Acetylation of **1** gives a diacetate (**2**) whose IR spectrum does not show hydroxyl absorption.

It seems plausible that the third oxygen atom of **1** is involved in an ether linkage. The ^{1}H NMR spectrum of **1** shows two tertiary methyl groups (δ 0.72 and 1.08), one methyl group (δ 1.43), protons (δ 2.68) on an epoxide ring, an AB quartet (δ 3.14 and 3.50, J = 11.0 Hz), assigned to the equatorial $-CH_2OH$ on C-4 of a tetracyclic diterpene backbone, and a signal at δ3.90 ($W_{1/2}$ = 16.0 Hz) indicative of a secondary hydroxyl group possibly with an equatorial configuration. The latter signals are shifted downfield (δ 4.93) on acetylation with one axial–axial (J = 10 Hz) and one axial–equatorial (J = 2.5 Hz) coupling constant. Comparison of the ^{1}H NMR spectra of sideroxol (**3**) [3] with that of the new product showed that the C-7 equatorial proton appeared as a triplet (δ 3.65, J = 2.5 Hz), whereas the C-7 axial proton of 'ucriol' appeared as a broad signal (δ3.90, $W_{1/2}$ = 16.0 Hz). Hence **1** and **3** are epimeric at C-7. Therefore, 'ucriol' has the structure and absolute configuration shown in **1**.

The structure and stereochemistry of **1** were fully confirmed by partial synthesis of **1** by the route **5** → **4** → **6** → **1**. The sodium borohydride reduction of **4** prior to