(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%.)

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UCRIOL, AN EPOXY-DITERPENE FROM *SIDERITIS SYRIACA*

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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

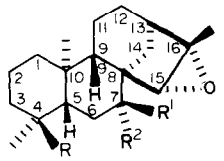
From the aerial part, and mainly from the corollas and inflorescence of *Sideritis syriaca* L. (*S. sicula* Ucria) [1] we have extracted eight new diterpenoids of the ent-kaurene–isokaurene [2] type. A new study of the petrol extract of the inflorescence of this plant has now allowed the isolation of 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

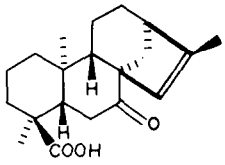
A careful chromatographic investigation of the mother liquors from the isolation of the major diterpenic constituents indicated the presence of a very small amount of a new diterpene. Ucriol (**1**), mp 185–186°, $C_{20}H_{32}O_3$, (analytical and mass spectra, *m/z* 320 $[M]^+$) gives a negative TNM 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**.

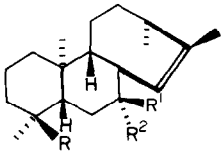
The structure and stereochemistry of **1** were fully confirmed by partial synthesis of **1** by the route **5** → **4** → **6** → **1**. The sodium borohydride reduction of **4** prior to



	R	R^1	R^2
1	CH_2OH	H	OH
2	CH_2OAc	H	OAc
3	CH_2OH	OH	H



4



	R	R^1	R^2
5	CH_2OH	OH	H
6	CH_2OH	H	OH

lithium aluminium hydride treatment to give **6**, supported the configuration ascribed [6] to C-7.

It is noteworthy that 'ucriol' is the second kaurene derivative (the first was candicandiol from *S. candicans* [7]) found in *Sideritis* sp. with a secondary hydroxyl group on C-7 in equatorial configuration, all the other diterpenes having an axial hydroxy group.

EXPERIMENTAL

Mps (Kofler block): uncorr. IR: nujol mull; ^{1}H NMR Varian EM (360)(1) and FT 80 (2), $CDCl_3$ TMS as a int. ref.; MS: 75 eV; CC: Si gel Merck (0.063–0.200). All the products gave satisfactory elemental analyses.

Plant material. Sideritis syriaca L. (*S. sicula* Ucria) was collected from the high summits of Madonie Mount (Sicily) at 1500 m above sea level. A specimen is deposited in the Herbarium of the Orto Botanico, University, Palermo.

Extraction of the diterpene. General details of extraction and separation of diterpenes from *S. syriaca* were described previously [2, 4]. The inflorescences (4.5 kg) were extracted in a Soxhlet for 75 hr with petrol (16 l.). The extract, after concn of the solvent gave a white crystalline ppt containing the major diterpenic constituents. From the filtrate a sticky residue was obtained after evaporation under vacuum. Chromatography on Si gel (Et_2O–EtOAc, 1 : 3) afforded 10 mg compound **1**. 'Ucriol' (**1**), mp 185–186° (from EtOAc), negative TNM test; IR ν_{max} cm^{-1}: 3350 (*br*) (OH); MS *m/z*: 320 [M]$^+$; ^{1}H NMR: δ 0.72 (3H, *s*, 4α-Me), 1.08 (3H, *s*, 10α-Me), 1.43 (3H, *s*, 16β-Me on epoxy ring), 2.86 (1H, *s*, H-15 on epoxy ring), 3.14 and 3.50 (2H, AB*q*, J = 11.0 Hz, 4β-CH_2OH), 3.90 (1H, *br*, $W_{1/2}$ = 16.0 Hz, 7β-H).

Diacetylucriol (**2**). Treatment of **1** (7 mg) with Ac_2O–pyridine as usual, gave **2** as an oil which could not be crystallized; IR ν_{max} cm^{-1}: no OH absorption; 1738 and 1250 (OAc); ^{1}H NMR: δ 0.82 (3H, *s*, 4α-Me), 1.07 (3H, *s*, 10α-Me), 1.40 (3H, *s*, 16β-Me on epoxy ring), 2.06 and 2.08 (6H, 2*s*, 2OAc), 2.84 (1H, *s*, H-15 on epoxy ring) 3.64 and 3.78 (2H, AB*q*, J = 11.0 Hz, 4β-CH_2OAc), 4.93 (1H, *dd*, J_{aa} = 10.0 Hz, J_{ae} = 2.5 Hz, 7β-H).

Partial synthesis of ent-15β,16β-epoxykaurane-7β,18-diol (**1**). Jones oxidation of sideridiol (ent-7α,18-dihydroxykaur-15-ene, **5**) gave ent-7-oxo-kaur-15-en-18-oic acid (**4**) [4], mp 214–215° (from EtOH–H_2O). Reduction of the keto acid (**4**) with $NaBH_4$ and then with $LiAlH_4$ afforded episideridiol (ent-7β,18-dihydroxykaur-15-ene) (**6**) [5], mp 197–198° (from MeOH–H_2O). ^{1}H NMR data for **4** and **6** have already been reported [4, 5].

The diol (**6**) (25 mg) in Et_2O (80 ml) was treated with *p*-nitroperbenzoic acid (40 mg) at room temp. for 24 hr. The soln was washed with aq. Na_2CO_3, dried and evaporated. The epoxide (18 mg), mp 185–186° (from EtOAc), was identical to the natural product (IR and ^{1}H NMR spectra superimposable).

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