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DITERPENES FROM *SIDERITIS THEEZANS*

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Key Word Index—*Sideritis theezans*; Labiatae; tetracyclic diterpenes; new isokaurene derivative; epoxy-isolinearol.

Continuing our researches on the diterpenes from the genus *Sideritis*, we report here on *Sideritis theezans* Boiss. *et* Heldr., a species growing in Greece.

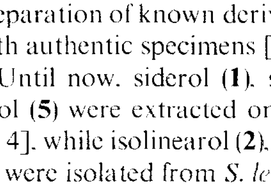
The light petrol extract was chromatographed on a silica gel column. The fractions eluted in the order contained siderol [1] (**1**), *iso*linearol [2, 3] (**2**), *iso*sidol [2, 3] (**3**), sideridiol [1] (**4**), sideroxol [4] (**5**), a new diterpene shown to be as epoxy-*iso*linearol (**6**), and *iso*foliol [2, 3] (**7**).

The already known compounds were identified on the basis of their m.p., IR, MS and NMR, the preparation of known derivatives, and comparison with authentic specimens [1–4].

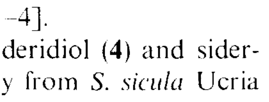
Until now, siderol (**1**), sideridiol (**4**) and sideroxol (**5**) were extracted only from *S. sicula* Ucria [1, 4], while isolinearol (**2**), *iso*foliol (**7**) and *iso*sidol (**3**) were isolated from *S. leucantha* Cav. [2, 3].

The unknown product (**6**), m.p. 118–120° (from EtOAc), has $C_{22}H_{34}O_5$ (MS, M^+ 378). Its NMR spectrum shows signals for two tertiary methyls, one acetyl, two $-C\underline{H}OH$ and one $C\underline{H}_2OAc$, whose chemical shifts are identical with those we observed for *iso*linearol: on the other hand, the two signals for the allylic methyl and the olefinic proton are substituted with a methyl and a proton signals on epoxide ring, at 1·41 δ and 3·10 δ respectively.

Hence, the structure (**6**) is 3α,7β-dihydroxy-18-acetoxy-15,16-epoxy-(−)-kaurane and the trivial name epoxy-*iso*linearol is proposed for this new diterpene. The above structure was fully confirmed by the synthesis of (**6**), by epoxidation of *iso*linearol with *p*.nitroperbenzoic acid.



	R'	R''	R
(**1**)	H	OH	OAc
(**2**)	OH	OAc	OH
(**3**)	OAc	OH	OH
(**4**)	H	OH	OH
(**7**)	OH	OH	OH



	R'	R''
(**5**)	H	OH
(**6**)	OH	OAc

EXPERIMENTAL

M.ps are uncorrected. IR: Nujol mull. NMR: 60 MHz, $CDCl_3$ soln with TMS as an internal standard. MS: 70 eV, direct inlet system. TLC: Si gel G, eluent: cyclohexane–EtOAc 1:1.

Extraction and separation. Air-dried aerial parts of *Sideritis theezans* (400 g) were milled and extracted in a Soxhlet apparatus with light petrol for 48 hr. The solvent was removed under reduced pressure and the residue chromatographed on a Si gel column (0·05–0·20 mm).

Elution with light petrol–Et_2O (75:25) gave siderol (300 mg), m.p. 152–153° (from light petrol.), R_f 0·75; m.p., IR and NMR identical with reported [1] data; m.m.p. did not depress.

The fraction eluted with light petrol–Et_2O (25:75) contained *iso*linearol (100 mg) and *iso*sidol (15 mg): the two products were separated repeating the chromatography on this fraction. *Iso*linearol, m.p. 185–186° (from EtOAc) (reported [2, 3] 187–188°), R_f 0·60, MS M^+ 362, gave IR and NMR (DMSO) data identical with those reported [2, 3]: direct comparison with IR and NMR (DMSO) spectra of authentic *iso*linearol proved the identity of the products; by alkaline hydrolysis it yielded *iso*foliol [2, 3], m.p. 236–238°; by acetylation triacetyl-*iso*foliol [2, 3] was obtained, m.p. 135–136°. *Iso*sidol, m.p. 180–181° (from cyclohexane–Et_2O) (reported [2, 3] 181–183°), R_f 0·45; TNM reaction: positive; NMR: 3·12 δ (*q*, *J* 12 Hz, CH_2OH), 4·88 δ (*m*, H-3); by acetylation it gave triacetyl-*iso*foliol [2, 3], m.p. 135–136°.

The light petrol–Et_2O (5:95) fraction yielded sideridiol (100 mg), m.p. 196–197° (form MeOH–H_2O), R_f 0·60; m.p., IR and NMR identical with reported [1] data; m.m.p. did not depress.

The Et_2O fraction eluted sideroxol (40 mg), m.p. 245–246° (from AcOEt), R_f 0·35; m.p., IR, MS and NMR identical with reported [1] data; m.m.p. did not depress. Elution with Et_2O–EtOAc (75:25) yielded epoxy-*iso*linearol (30 mg). Elution with EtOAc-MeOH (95:5) gave *iso*foliol (15 mg), m.p. 236–238° (from EtOH–H_2O) (reported [2, 3] 230–231°), R_f 0·25; its IR spectrum was superimposable to that of the product (m.p. 236–238°) obtained by desacetylation of *iso*linearol: by acetylation it yielded triacetyl-*iso*foliol, m.p. 135–136° (from EtOH–H_2O) (reported [2, 3] 134–135°).

Epoxy-iso*linearol.* M.p. 118–120° (from AcOEt), R_f 0·35. MS: 378 *m/e* (M^+). IR: 3450 and 3300 cm^{-1} (OH), 1730 and 1240 cm^{-1} (acetate). NMR: 0·75 and 1·02 δ (*s*, *t*. Me), 1·41 δ (*s*, Me on epoxide ring), 2·06 δ (*s*, OCOMe), 3·10 δ (*s*, H-15 on epoxide ring), 3·37 δ (*m*, H-3), 3·70 δ (*m*, H-7), 3·97 δ (*s*, C<u>H</u>$_2$OAc). The product was also prepared by treatment of *iso*linearol with *p*-nitroperbenzoic acid, as described for similar derivatives [4].

Iso*linearol*. The NMR spectrum, recorded in $CDCl_3$, gave the following signals: 0·76 and 1·05 δ (*s*, *t*, Me), 1·71 δ (*d*, *J* 1·5 Hz, allylic Me), 2·07 δ (*s*, OCOMe), 3·37 δ (*m*, H-3), 3·65 δ (*m*, H-7), 3·99 δ (*s*, C<u>H</u>$_2$OAc), 5·48 δ (broad *s*, H-15). Small differences are therefore noted in comparison with the spectrum in DMSO-d_6 [2, 3].

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FLAVONOIDS FROM *DALBERGIA CEAREANSIS*[*]

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Key Word Index—*Dalbergia cearensis*; Leguminosae; neoflavonoids; isoflavonoids; 2,5-dihydroxy-4-methoxybenzophenone.

Herbarium samples of *Dalbergia cearensis* Ducke and *D. frutescens* (Vell.) Britt. (= *D. variabilis* Vog.) are very similar. In the field, however, the species are easily distinguished, since *D. cearensis* is a tree and *D. frutescens* a scandent shrub [2]. The present phytochemical examination is based on a sample of trunk wood, collected by Dr. F. J. de Abreu Matos, Universidade Federal do Ceará, a former collaborator of Dr. A. Ducke, at Acaraú, Ceará State, from a small tree (height 4·5 m, diameter of heartwood 9 cm). The correctness of the identification was confirmed by Dr. D. de Andrade Lima, Universidade Federal de Pernambuco, by comparison of herborized material. Among the seven compounds isolated, (*S*)-4-methoxydalbergione [3], dalbergin [4], formononetin [1], and (±)-demethylhomopterocarpin [1] had already been obtained from other species during the current study of *Dalbergia* and *Machaerium*, and were identified by direct comparison with authentic samples.

One of the additional compounds was identical in all respects to (*S*)-mucronulatol [5, 6] with exception of the antipodal ORD curve and must thus represent the, as yet unreported, (*R*)-mucronulatol (**1a**). The racemate of mucronulatol occurs in *D. frutescens* [5].

Careful analysis of the τ 5·3–5·9 region [7] of the PMR spectrum (τ 5·32, H_{eq}-2; 5·50 H_{ax}-2; 5·81, H-3) revealed still another compound $C_{15}H_8O_2.OH(OMe)_3$, to be isoflavanone (**2a**). Retroaldol cleavage led to MS peaks compatible with monohydroxylation of ring *A* and trimethoxylation of ring *B*. The typical aromatic ABX PMR pattern, which included a low field d (τ 2·1, *J* 8·5 Hz), and UV NaOAc shifts placed the OH at C-7. One of the ring *B* hydrogens is situated at a relatively deprotected site (τ 3·00, *J* 8·5 Hz), vicinal to the other (τ 3·20, *J* 8·5 Hz) hydrogen. This evidence is in good agreement with the structure of 3′-*O*-methylvio-

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