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TEUSCORDINON, A FURANOID DITERPENE FROM *TEUCRIUM SCORDIUM*

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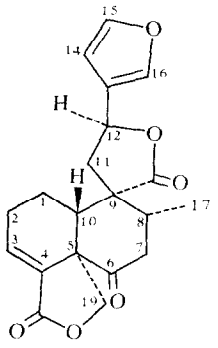
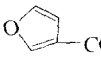
Key Word Index—*Teucrium scordium* var. *scordium*; Lamiaceae; teuscordinon; new furanoid diterpene; clerodane type.

From the aerial parts of Bulgarian *Teucrium scordium* (Lamiaceae) we have isolated a new furanoid diterpene which was named teuscordinon (**1**). The IR spectrum of **1** contained two intensive bands for two γ-lactones (1775 and 1750 cm^{-1}), a keto group (1725 cm^{-1}), a double bond (1660 cm^{-1}) and a furan ring (1510 and 885 cm^{-1}). According to the MS this compound had the molecular formula $C_{20}H_{20}O_6$. The ^1H NMR spectrum of **1** showed that the oxygen functions were two γ-lactones and a β-substituted furan ring (Table 1). As shown in Table 1, the 7-H_2 of **1** was observed at the lower field (7α-H, δ 3.36 *dd*; 7β-H, 2.44, *dd*, J = 14 Hz) which showed unambiguously that the keto group was at C-6 [1]. The proton at C-3 appeared as a double doublet at δ 6.88 (J = 8.2 Hz). The methylene protons at C-19 resonated at 4.13 and 4.93 (1 H each AB q, J = 12 Hz) which showed that the C(5)–C(19) and C(9)–C(20) bonds were in a *cis* relationship, i.e. were α-oriented [1,2]. By a similar argument, the chemical shift of the C-10 proton (δ 2.17) required a *trans* arrangement of C-10 H and the C(9)–C(20) bonds, i.e. β-configuration at C-10. The stereochemistry at the other chiral centre was deduced by use of Eu(fod)$_3$ and by careful spin decoupling (Table 1).



1

EXPERIMENTAL

Dried plant material (2 kg) was extracted with Me_2CO and after evapn the residue was treated as in ref. [3]. The $CHCl_3$ extract (18 g) was passed through a Si gel column. Elution with $CHCl_3$–MeOH (99.5:0.5) yielded a single compound (30 mg). Et_2O–Me_2CO (9:1) crystallization gave **1** as colourless crystals, mp 235°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775 (γ-lactone), 1725 (C=O), 1510 and 885 (furan ring); ν_{max}^{KBr} cm^{-1} 1775 and 1750 (two γ-lactone). MS (70 eV) *m/e* (rel. int.): 356.126 (M^+, 15) ($C_{20}H_{20}O_6$); 326 (6) (M–CH_2O); 178 (48); 95 (37) (); 83 (100).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-84.1 \quad -88.0 \quad -101.8 \quad -200.0}$$

(c = 1.2, dioxane).

Table 1. ^1H NMR spectral data of compound **1** and effect of the addition of the shift-reagent Eu(fod)$_3$ (270 MHz, $CDCl_3$, TMS as internal standard)

1α-H	1.63 *dddd*	0.19*	11-H	2.3–2.6 *m*	
1β-H	2.17 *m*		12-H	5.47 *dd(br)*	0.10*
2-H	2.3–2.6 *m*		14-H	6.43 *s(br)*	0.03*
3-H	6.88 *dd*	0.38*	15-H	7.48 *dd*	0.01*
7α-H	3.36 *dd*	0.32*	16-H	7.51 *s(br)*	0.03*
7β-H	2.44 *dd*	0.25*	17-H	1.19 *d*	0.10*
8β-H	2.17 *m*	0.15*	19-H	4.93 *d*	0.37*
10-H	2.17 *m*	0.15*	19-H	4.13 *d*	0.34*

* Δ-values after addition of 0.1 equivalents of Eu(fod)$_3$.

J (Hz): 1α,1β = 12; 1α,2α = 4.5; 1α,2β = 1α,10β = 12; 2,3 = 8; 2',3 = 2; 7α,7β = 14; 7α,8β = 13; 7β,8β = 5; 11,12 = 8.5; 14,15 = 15,16 = 1.7; 19,19' = 12.

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TRITERPENOIDS OF *SCOPARIA DULCIS*

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Key Word Index—*Scoparia dulcis*; Scrophulariaceae; friedelin; glutinol; α-amyrin; ifflaionic acid; dulcioic acid.

Abstract—The triterpenoids of *Scoparia dulcis* were identified as friedelin, glutinol, α-amyrin, betulinic acid, ifflaionic acid and dulcioic acid.

Scoparia dulcis L. (Scrophulariaceae) is reputed for its medicinal property. 'Amellin', which has been used in India as an antidiabetic principle, was obtained from the fresh plant [1, 2]. The plant is reported to be used as a cure for hypertension in Taiwan [3]. Several groups of investigators carried out phytochemical work on this plant and reported the isolation of hexacosanol, tritriacontane, sitosterol, D-mannitol, three unidentified compounds, dulciol, dulciolone and scoparol [4–6], betulinic acid, ifflaionic acid and benzoxazolinone [7]. The present communication reports the isolation and characterization of the three unidentified compounds in addition to a new triterpenic acid designated as dulcioic acid (**1**).

Repeated Si gel column chromatography of a petrol extract of the dried and powdered whole plant led to the isolation of pure crystalline compounds SD-I, SD-II, SD-III, SD-IV and a mixture of SD-V and SD-VI. SD-V and SD-VI could be separated by esterification with CH_2N_2 followed by chromatography. Compound SD-1, mp 264–266° was identical with friedelin (mmp, IR, ^{1}H NMR, MS). By comparison of the physical data, dulciolone, previously isolated from the plant [5, 6], seemed to be identical with friedelin. SD-II, mp 209–210° was characterized as glutinol by comparison of its mass and ^{1}H NMR spectra with those of an authentic sample. The ^{13}C NMR spectrum of this compound was recorded and carbon chemical shifts were assigned by multiplicity information obtained from single frequency off-resonance spectra, known chemical shift rules [8] and by comparison of shift data of other triterpenes [9–11]. The reported physical data of dulciol [5–6] indicated its identity with glutinol. SD-III, mp 184–186°, whose physical data compared well with those of scoparol was identical with α-amyrin. SD-IV was characterized as betulinic acid. SD-V', 180–182°, showed positive Liebermann–Burchard and tetranitromethane tests. The IR spectrum showed absorbance at 1730 and 1695 cm^{-1} indicating the presence of an ester carbonyl and a ketonic function. The ^{1}H NMR spectrum displayed signals attributable to seven methyls, a carbomethoxy group, a trisubstituted double bond and two α-protons to a carbonyl group. The mass spectrum showed peaks at *m/e* 468 (M^+), 262 (retro Diels–Alder fragment *a*, base peak) and 247 (*a* − Me) characteristic of methyl ifflaionate (**2**) [7]. On saponification, SD-V' readily yielded an acid, mp 265–266°, which was found to be identical with an authentic sample of ifflaionic acid (**5**) (mp, mmp, TLC, IR, MS).

SD-VI' (**3**), mp 192–194°, formed an acetate (**4**), mp 258–259°, which showed in its ^{1}H NMR spectrum signals assignable to seven methyls, a carbomethoxy group, an acetoxy methyl, a trisubstituted double bond and a carbonyl proton. The MS of **3** showed a fragmentation