Arctigenin (5).Colourless crystals, mp 102°; ^{1}H NMR ($CDCl_3$): 6.64 (*d*, H-2), 6.82 (*d*, H-6), 6.60 (*dd*, H-7), 2.96 and 2.91 (*dd*, H-8), 2.57 (*ddd*, H-2'), 6.46 (*d*, H-5'), 6.74 (*d*, H-6'), 6.55 (*dd*, H-7'), 2.64 and 2.53 (*dd*, H-8'), 2.49 (*ddd*, H-9'), 3.89 (*dd*, OMe), 3.86, 3.82, 3.81 (*s*, OH), 5.52 (*br s*); (J [Hz]: 2, 6 = 2',6' = 2; 5, 6 = 5', 6' = 8; 7_1, 7_2 = 14; 7,8 = 4; 8,8' = 7; 7_1', 7_2' = 13; 7',8' = 6; 8',9' = 7; 9_1',9_2' = 9).

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2-DEOXYCHAMAEDROXIDE, A NEO-CLERODANE DITERPENOID FROM *TEUCRIUM DIVARICATUM*

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Key Word Index—*Teucrium divaricatum*; Labiatae; neo-clerodane diterpenoids.

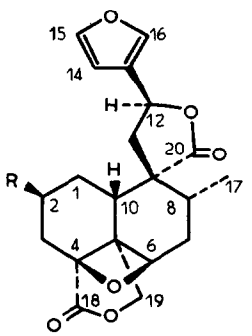
Abstract—A new neo-clerodane diterpenoid, 2-deoxychamaedroxide, has been isolated from the aerial parts of *Teucrium divaricatum* subsp. *canescens*. Also identified were the previously known diterpenoids teuflin, teucrin H_2, teuflidin, teucrins A, F and G, 6β-hydroxy-teuscordin, montanin D and dihydroteugin. The structure of 2-deoxychamaedroxide, (12*S*)-4β,6β; 15,16-diepoxy-neo-clerodane-13(16),14-diene-18,19; 20,12-diolide, was established mainly by spectroscopic means.

INTRODUCTION

In continuation of our studies on neo-clerodane diterpenoids from *Teucrium* species [1, 2], we have now investigated *T. divaricatum* Sieber *ex* Boiss. subsp. *canescens* (Celak.) Holmboe. From the aerial parts of this plant we have isolated 10 neo-clerodane diterpenoids, nine of which are the already known teuflin [3], teucrin H_2 [4], teuflidin [5], teucrins A [6, 7], F and G [8, 9], 6β-hydroxyteuscordin [10], montanin D [11] and dihydroteugin [7, 12], and the tenth is a new substance, 2-deoxychamaedroxide (**1**), whose structure has now been established.

RESULTS AND DISCUSSION

2-Deoxychamaedroxide (**1**) had a molecular formula $C_{20}H_{22}O_6$ and its IR spectrum was devoid of hydroxyl absorptions and was consistent with the presence of a furan ring (3140, 1505, 875 cm^{-1}) and γ-lactone groups (broad and strong absorption at 1770 cm^{-1}).



1 R= H

2 R= OH

3 R= OAc

However, it was the ^{1}H NMR spectrum of 2-deoxychamaedroxide (Table 1) that provided the most information and established for this compound the structure and relative configuration depicted in 1. This ^{1}H NMR spectrum (recorded in deuteriochloroform solution) was very similar with that reported for chamaedroxide (2, recorded in pyridine-d_5 solution, see Table 1), a neo-clerodane diterpenoid previously isolated from *T. chamaedrys* and whose structure is well known from an X-ray diffraction analysis [13]. In fact, the ^{1}H NMR spectra of compound 1 and the acetyl derivative of chamaedroxide 3 (both recorded in deuteriochloroform solution, see Table 1) were almost identical in the chemical shifts and coupling values corresponding to the H-6α, 2H-11, H-12, H-14, H-15, H-16, Me-17 and 2H-19 protons (Table 1). The only difference was the absence in the former of the signals due to the C-2β acetoxyl group of the latter.

The 12*S*-configuration of compound 1 was in agreement with NOE experiments, since irradiation of the Me-17 protons (δ 0.90) caused NOE enhancement in the signals of the H-14 (δ 6.37, 3.4%) and H-16 (δ 7.44, 1.2%) protons, whereas the signal of the C-12 proton (δ 5.51) was not affected. This behaviour clearly established that the furan ring moiety and the Me-17 group of compound 1 are on the same side of the plane defined by the C-20, C-12 γ-lactone ring [14].

Table 1. ^{1}H NMR data of compounds 1–3 (TMS as internal standard)

	1*	2†	3†
H-2α	§	4.18 *m*	4.72 *m*
H-6α	5.17 *dd*	5.17 *dd*	5.15 *dd*
H-10β	2.80 *dd*	3.25 *t*	‡
H_A-11	2.32 *dd*	2.41 *dd*	2.33 *dd*
H_B-11	2.79 *dd*	2.95 *dd*	2.76 *dd*
H-12	5.51 *ddd*	5.62 *dd*	5.49 *dd*
H-14	6.37 *dd*	6.54 *m*	6.36 *m*
H-15	7.46 *t*	7.73 *t*	7.46 *m*
H-16	7.44 *ddd*	7.65 *m*	7.46 *m*
Me-17	0.90 *d*	0.88 *d*	0.90 *d*
H_A-19	4.29 *d*	4.43 *d*	4.28 *d*
H_B-19	4.46 *d*	4.56 *d*	4.42 *d*
OAc	–	–	2.04 *s*
J (Hz)			
6α, 7α	7.4‖	7.5	6.5‖
6α, 7β	6.1‖	6	6‖
8β, 17	7.2	7	7
10β, 1α	13.5	10	‡
10β, 1β	5.4	10	‡
11A, 11B	13.3	13.5	13.5
11A, 12	4.3	5	4.5
11B, 12	8.5	8	8
12, 16	1.2	‡	‡
14, 15	1.7	‡	‡
14, 16	0.8	‡	‡
15, 16	1.7	‡	‡
19A,19B	11.3	11	11.5

*At 300 MHz. $CDCl_3$ solution.

†Taken from ref. [13] (at 100 MHz; 2 in pyridine-d_5 solution, 3 in $CDCl_3$ solution).

‡Values not given in ref. [13].

§Overlapped signal.

‖These assignments may be interchanged.

The absolute configuration of 2-deoxychamaedroxide (1) was not ascertained. However, compound 1 is believed to belong to the neo-clerodane series like all the other diterpenoids co-occurring in the same species (see above). Moreover, all the diterpenoids until now isolated from *Teucrium* species [15] belong to the neo-clerodane series. The similarity between the $[\alpha]_D$ values of chamaedroxide (2, +37.1°) [13] and compound 1 (+40.0°) also supported this conclusion.

EXPERIMENTAL

For general details on methods, see refs [1, 2, 7, 9, 12–14]. Plant materials were collected in April 1986 near the Monastery of Stavrovouni (Larnaca, Cyprus) and voucher specimens were deposited in the Herbarium of the 'Dipartimento di Biologia', University of Milan, Italy.

Extraction and isolation of the diterpenoids. Dried and finely powdered *T. divaricatum* subsp. *canescens* aerial parts (140 g) were extracted with Me_2CO (1.5 l) at room temp. for a week. The extract (10 g) was chromatographed on a silica gel column (Merck, No. 7734, deactivated with 15% H_2O, 250 g) eluted with *n*-hexane, *n*-hexane–EtOAc mixtures and EtOAc. Elution with *n*-hexane–EtOAc (1:1) successively gave 2-deoxychamaedroxide (1, 7 mg), teuflin (30 mg) [3] and teucrin H_2 (15 mg) [4]. Elution with EtOAc–*n*-hexane (2:1) yielded the following compounds in order of increasing chromatographic polarity: teuflidin (12 mg) [5], teucrin F (3 mg) [8, 9], teucrin G (4 mg) [8, 9], 6β-hydroxyteuscordin (10 mg) [10] and montanin D (30 mg) [11]. Finally, elution with EtOAc successively yielded dihydroteugin (70 mg) [7, 12] and teucrin A (500 mg) [8, 9].

The previously known diterpenoids (see above) were identified by their physical (mp, $[\alpha]_D$) and spectroscopic (IR, ^{1}H NMR, MS) data and by comparison (mmp, TLC) with authentic samples.

2-Deoxychamaedroxide (1). An amorphous powder which melted at 85–89°; $[\alpha]_D^{22}$ + 40.0° ($CHCl_3$; *c* 0.105); IR ν_{max}^{KBr} cm^{-1}: 3140, 2950, 2880, 1770 (*br*), 1505, 1455, 1365, 1335, 1160, 990, 875; ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 358 $[M]^+$ (4), 330 (2), 220 (9), 187 (9), 161 (20), 119 (21), 105 (36), 95 (82), 94 (100), 91 (39), 81 (57), 77 (30), 55 (37). (Found: C, 66.84; H, 6.26. $C_{20}H_{22}O_6$ requires: C, 67.02; H, 6.19%.)

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A NEW DITERPENOID FROM *ERICAMERIA LARICIFOLIA*

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Key Word Index—*Ericameria laricifolia*; Asteraceae; Astereae; Solidagininae; diterpenoid acids; labdanes; grindelanes.

Abstract—An acid fraction of the methylene chloride extract of *Ericameria laricifolia* gave, in addition to four known grindelanes, a new diterpenoid acid possessing an *ent*-labdane skeleton. Its structure, based on the spectral properties of its methyl ester derivative, has been determined as 15-succinyloxy-*ent*-labd-13*E*-en-8β-ol.

INTRODUCTION

As part of our phytochemical investigations of the genus *Ericameria* (Asteraceae, Astereae) from the southwestern U.S.A. [1], we have now examined the resin acid constituents of *Ericameria laricifolia* (Gray) Shinners from New Mexico. *Ericameria*, a new world genus of perhaps 12 species, is often treated as a section of the genus *Haplopappus*. *E. laricifolia* is a resinous shrub that grows on desert hillsides from eastern California to western Texas. The chemistry of *Ericameria* is largely unknown. Four taxa were reported to produce flavonoid aglycones and glycosides [2, 3] as well as labdane diterpenoid acids [1]. In this paper we describe the isolation and characterization of a new and four previously reported labdanoids from *E. laricifolia*.

RESULTS AND DISCUSSION

The methylene chloride extract of the above-ground biomass gave an ether soluble fraction from which the sodium carbonate-soluble acid fraction was separated and methylated. Separation of the methylated product chromatographically yielded the new labdane **1b** and four known grindelane methyl esters: methyl 6-oxo-17-acetoxy-(**2b**) [4], 17-acetoxy-(**3b**) [4], 18-acetoxy-(**4b**) [1] and 17-isobutyroxy-(**5b**) [4] grindelate, identified by TLC and ^{1}H NMR spectral comparisons with authentic samples. Compounds **3b** and **4b** have very similar R_f vlues and were not separated from one another, but the amount of each present in the mixture of two was clear by ^{1}H NMR.

Structure of compound **1b**

The IR ($CHCl_3$) spectrum of **1b** showed absorption for hydroxyl (3520 cm^{-1}), ester (1730 and 1155 cm^{-1}), =CH- (3010 and 838 cm^{-1}), -CH_2CO- (1405 cm^{-1}) and -$C(Me)_2$- (1380 and 1360 cm^{-1}) groups. The EI mass spectrum of **1b** allowed deduction of the structure except for stereochemistry. The molecular ion peak at *m/z* 422, which was barely discernible, was deduced from peaks at *m/z* (rel. int.) 291 $[M-O_2CCH_2CH_2COOMe]^+$ (1.7), 290 $[M-HOOCCH_2CH_2COOMe]^+$ (7.2), 275 $[290-Me]^+$ (5.1), 272 $[290-H_2O]^+$ (8.5) and 257 $[290-Me-H_2O]^+$ (8.8). These peaks, together with an intense peak at *m/z* 115 $[O^+\equiv CCH_2CH_2COOMe]$ (94.4%) suggested that **1b** was a methyl succinate derivative of a diterpene