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NEO-CLERODANE DITERPENOIDS FROM *TEUCRIUM MICROPODIOIDES*

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Key Word Index—*Teucrium micropodioides*; Labiatae; neo-clerodane derivatives; teumicropin; 3-acetylteumicropin; teumicropodin; deacetylteupyrenone; 3-deacetyl-20-*epi*-teulanigin.

Abstract—From the aerial parts of *Teucrium micropodioides* five new neo-clerodane diterpenoids, teumicropin, 3-acetylteumicropin, teumicropodin, deacetylteupyrenone and 3-deacetyl-20-*epi*-teulanigin, have been isolated. The structures of these substances were established by chemical and spectroscopic means and by correlation with known compounds.

INTRODUCTION

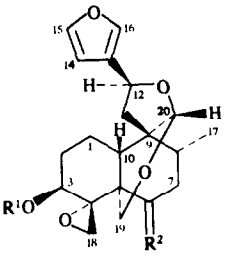
A large number of diterpenoids with the clerodane skeleton have been isolated from plants in the last few years. Interest in these compounds has been stimulated by their biological activity as insect antifeedants and as antifungal, antitumour and antimicrobial agents. The *Teucrium* species (family Labiatae) have afforded a great number of these compounds [1].

In continuation of our studies on neo-clerodane diterpenoids from the *Teucrium* species [1], we have investigated *T. micropodioides* Rouy, a species which grows in limited areas of Cyprus. From the aerial parts of this plant five new diterpenoids, 3-acetylteumicropin (**1**), teumicropin (**3**), deacetylteupyrenone (**5**), teumicropodin (**6**) and 3-deacetyl-20-epi-teulanigin (**9**), have been isolated and their structures established by chemical and spectroscopic means and by correlation with previously known substances.

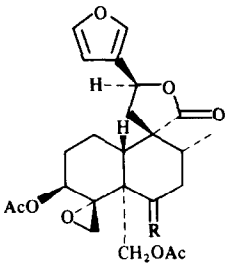
RESULTS AND DISCUSSION

The first of the new diterpenoids isolated from *T. micropodioides*, 3-acetylteumicropin (**1**), had a molecular formula $C_{22}H_{28}O_7$ and the ^{1}H NMR spectrum (Table 1) showed characteristic signals for a β-substituted furan ring, a 4α,18 oxirane ring, a 3β-acetoxyl function and an acetal group between the C-20 and the C-12 and C-19 carbon atoms identical with those found in teupyrenone (**2**), a neo-clerodane diterpenoid previously isolated from *T. pyrenaicum*, the structure and absolute configuration of which have been firmly established [2, 3]. In addition, the IR and ^{1}H NMR spectra of compound **1** revealed the presence of a 6β-hydroxyl group (ν_{OH} 3470 cm^{-1}; $\delta_{H\text{-}6\alpha}$ 3.52, *t*, $J_{6\alpha,7\alpha} = J_{6\alpha,7\beta} = 2.6$ Hz). Since chromium trioxide–pyridine oxidation of 3-acetylteumicropin (**1**) yielded a compound identical in all respects with teupyrenone (**2**), the structure and absolute configuration depicted in **1** were firmly established for this new diterpenoid.

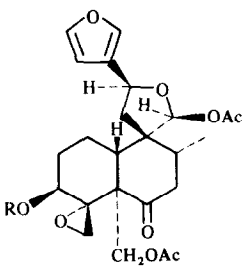
In addition to the chemical correlation of 3-acetylteumicropin (**1**) with teupyrenone (**2**), its 12*S*- and 20*S*-configurations were also in agreement with NOE experiments, since irradiation of the Me-17 protons produced NOE enhancement in the signals of the C-14, C-16 and C-20 protons, whereas the signal of the C-12 proton was not affected (Table 2) [3, 4].



	R¹	R²
1	Ac	αH, βOH
2	Ac	O
3	H	αH, βOH
4	Ac	αH, βOAc
5	H	O



	R
6	αOH, βH
7	αOAc, βH
8	O



	R
9	H
10	Ac

Table 1. ^{1}H NMR data of compounds **1**, **3**–**7** and **9** ($CDCl_3$, TMS as int. standard)*

	1	**3**	**3**†	**4**	**5**	**6**	**7**	**9**
H-2β	‡	‡	1.78 *qd*	‡	‡	‡	‡	‡
H-3α	5.24 *dd*	4.02 *dd*	4.45 *dd*	5.22‡	3.99 *dd*	5.35 *dd*	5.41 *dd*	4.16 *dd*
H-6α	3.52 *t*	3.53 *t*	3.83 *t*	4.46 *t*	—	—	—	—
H-6β	—	—	—	—	—	3.71 *brdd*	4.85 *brdd*	—
H-7α	1.97 *td*	‡	‡	‡	2.20 *dd*	2.14 *dd*	‡	3.00 *t*
H-7β	‡	‡	1.88 *ddd*	‡	2.96 *dd*	‡	‡	‡
H-8β	2.08 *m*	‡	2.38 *m*‡	‡	‡	‡	‡	‡
H-10β	‡	‡	2.72 *dd*	‡	‡	‡	‡	‡
H_A-11	2.14 *dd*	‡	2.23 *d*	2.16 *dd*	2.01 *dd*	2.38 *d*	2.38 *d*	‡
H_B-11	2.20 *dd*	‡		2.19 *dd*	2.41 *dd*			2.42 *dd*
H-12	5.21 *dd*	5.22 *dd*	5.42 *t*	5.22 ‡	5.08 *dd*	5.36 *dd*	5.37 *t*	5.00 *t*
H-14	6.41 *dd*	6.42 *dd*	6.70 *dd*	6.41 *dd*	6.37 *dd*	6.38 *dd*	6.37 *dd*	6.42 *dd*
H-15	7.40 *t*	7.41 *t*	7.68 *t*	7.41 *t*	7.40 *t*	7.44 *t*	7.41 *m*‡	7.39 *m*‡
H-16	7.42 *m*	7.42 *m*	7.83 *m*	7.42 *m*	7.41 *m*	7.45 *m*	7.41 *m*‡	7.39 *m*‡
Me-17	0.99 *d*	0.99 *d*	0.96 *d*	0.97 *d*	1.04 *d*	1.03 *d*	0.98 *d*	1.30 *d*
H_A-18	3.17 *d*	3.30 *d*	3.91 *d*	2.51 *d*	2.42 *d*	2.84 *d*	2.63 *d*	2.82 *d*
H_B-18	3.36 *d*	3.38 *d*	3.95 *d*	3.15 *d*	3.09 *d*	3.09 *d*	2.85 *d*	3.17 *d*
H_A-19	3.34 *d*	3.32 *d*	3.61 *d*	3.40 *d*	4.06 *d*	4.67 *brd*	4.50 *brd*	4.59 *d*
H_B-19	4.25 *d*	4.16 *d*	4.56 *d*	4.27 *d*	4.38 *d*	4.89 *d*	5.05 *d*	4.79 *d*
H-20	5.10 *s*	5.10 *s*	5.38 *s*	5.09 *s*	5.11 *s*	—	—	6.31 *s*
OAc	2.03 *s*	—	—	2.09 *s*	—	2.12 *s*	2.07 *s*	2.14 *s*
	—	—	—	2.03 *s*	—	2.02 *s*	1.93 *s*	2.04 *s*
	—	—	—	—	—	—	1.93 *s*	—
J (Hz)								
1α,2β	‡	‡	12.0	‡	‡	‡	‡	‡
1β,2β	‡	‡	3.0	‡	‡	‡	‡	‡
2α,2β	‡	‡	12.0	‡	‡	‡	‡	‡
2α,3α	3.4	3.7	3.7	‡	4.6	5.1	5.0	4.8
2β,3α	12.0	12.5	12.0	‡	11.9	11.7	11.0	11.6
6α,7α	2.6	2.6	2.6	2.6	—	—	—	—
6α,7β	2.6	2.6	2.6	2.6	—	—	—	—
6β,7α	—	—	—	—	—	11.4	12.0	—
6β,7β	—	—	—	—	—	3.9	4.8	—
7α,7β	12.8	‡	14.9	‡	15.6	12.3	‡	15.0
7α,8β	12.8	‡	‡	‡	3.3§	12.3	‡	15.0
7β,8β	‡	‡	4.8	‡	10.4§	‡	‡	‡
8β,17	6.4	6.4	6.9	6.2	7.3	6.6	6.6	6.9
10β,1α	‡	‡	12.8	‡	‡	‡	‡	‡
10β,1β	‡	‡	5.0	‡	‡	‡	‡	‡
11A,11B	13.4	‡	0	13.5	13.5	0	0	13.5
11A,12	9.8	10.1	8.6	8.4	8.9	8.5	8.5	8.4
11B,12	6.4	6.5	8.6	8.4	7.5	8.5	8.5	8.4
14,15	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.6
14,16	0.9	1.0	0.7	0.7	1.1	0.8	0.9	1.0
15, 16	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.6
18A,18B	4.7	4.0	5.7	4.2	4.7	3.8	4.2	5.5
19A,19B	13.7	12.8	13.2	13.6	11.2	13.3	12.3	12.1
19A,6β	—	—	—	—	—	<0.4	<0.4	—

*All these assignments have been confirmed by double resonance experiments.
†In pyridine-d_5 solution.
‡Overlapped signal.
§The ring B of compound **5** possesses a boat conformation, see refs [5, 6].

The deacetyl derivative of compound **1**, teumicropin (**3**), was also present in the acetone extract of *T. micropodioides*. The ^{1}H NMR spectrum of this substance (**3**, Table 1) was almost identical with that of **1**, the only differences being consistent with the absence of the 3β-acetyl group (no acetoxyl signal, up-field resonance of the C-3α proton, see Table 1). Acetic anhydride–pyridine treatment of compounds **1** and **3** yielded the same derivative (**4**), thus establishing for teumicropin the structure and absolute configuration depicted in **3**. Moreover, the 12*S*- and 20*S*-configurations of this diterpenoid were also in agreement with NOE experiments (Table 2) [3, 4].

Another of the diterpenoids found in *T. micropodioides*

Table 2. NOE experiments on compounds **1**, **3**, **5**, **6** and **9**

	Irradiation (δ Me-17 protons)	Observed NOE enhancement (%)			
		H-12	H-14	H-16	H-20
1	0.99	0	2.6	0.6	9
3	0.96	0	3.2	0.6	7.6
5	1.04	0	2.4	0.5	13.3
6	1.03	0	4.5	1.7	—
9	1.30	0	2.6	1.8	0

Table 3. ^{13}C NMR chemical shifts of compound **6** ($CDCl_3$, TMS as int. standard)

C		C	
1	21.9 *t**	13	124.9 *s*
2	30.7 *t*	14	107.9 *d*
3	65.8 *d*	15	144.2 *d*
4	66.6 *s*	16	139.6 *d*
5	45.7 *s*	17	16.4 *q*
6	72.7 *d*	18	42.9 *t*
7	33.3 *t*	19	61.2 *t*
8	38.2 *d*	20	175.6 *s*
9	50.9 *s*	OAc	171.0 *s*
10	51.5 *d*		169.2 *s*
11	43.1 *t*		21.1 *q*
12	71.4 *d*		20.7 *q*

*SFORD multiplicity.

was deacetylteupyrenone (**5**, $C_{20}H_{24}O_6$), which was transformed into teupyrenone (**2**, $C_{22}H_{26}O_7$) [2, 3] by acetic anhydride–pyridine treatment. As in the case of other 6-keto-neo-clerodan-20,12,19-acetal derivatives [5, 6], deacetylteupyrenone (**5**) possesses ring B in a boat conformation, with C-7 and C-10 at the flaps. This fact was clearly reflected in the coupling values between the C-7 methylene and C-8 methine protons (see Table 1).

Teumicropodin (**6**, $C_{24}H_{30}O_9$) showed an IR spectrum with hydroxyl (3480 cm^{-1}), furanic (3145, 3130, 1503, 875 cm^{-1}), γ-lactone (1760 cm^{-1}) and acetate (1740, 1230 cm^{-1}) absorptions. Its ^{1}H NMR spectrum (Table 1) revealed the presence of a β-substituted furan ring, two acetoxyl groups at the C-3β and C-19 positions of a clerodane hydrocarbon skeleton, a C-20, C-12 γ-lactone, a 4α,18-epoxide group and a secondary hydroxyl group at the C-6α position (geminal proton at δ3.71 *br dd*, $J_{6\beta,7\alpha}$ = 11.4 Hz, $J_{6\beta,7\beta}$ = 3.9 Hz, $J_{6\beta,19A}$ < 0.4 Hz) [2, 4, 5]. Moreover, the ^{13}C NMR spectrum of teumicropodin (**6**, Table 3) was in complete agreement [2, 4, 5] with a 3β,19-diacetoxy-4α,18; 15,16-diepoxy-6α-hydroxy-neo-clerodane-13(16), 14-dien-20,12*S*-olide structure (**6**), in which the 12*S*-stereochemistry was also supported by NOE experiments (Table 2) [3, 4].

In agreement with all the above conclusions, acetic anhydride–pyridine treatment of teumicropodin (**6**) yielded a triacetyl derivative (**7**), whereas chromium trioxide–pyridine oxidation gave a substance (**8**) identical in all respects (mp, mmp, $[\alpha]_D$, IR, ^{1}H NMR, MS) with a synthetic derivative of teulepicin, a neo-clerodane diterpenoid previously isolated from *T. lepicephalum* and whose structure (including its absolute configuration) is well known [7].

The last diterpenoid (**9**) isolated from *T. micropodioides* had a molecular formula $C_{24}H_{30}O_9$. Its spectroscopic data (Tables 1 and 2, and Experimental) suggested a structure such as **9** for this substance, which was confirmed by the fact that, on acetylation, it was transformed into a compound (**10**) identical in all respects with 20-*epi*-teulanigin, a diterpenoid with well known structure previously found in *T. lanigerum* [8]. In particular, the existence in compound **9** of a 3β-hydroxyl group was clearly established by the chemical shift of its geminal proton (δ4.16, *dd*), which appeared at higher field than in 20-*epi*-teulanigin (**10**, δ5.31, *dd*) [8]. Furthermore, the stereochemistry of the C-12 and C-20 centres of compound **9** was in complete agreement (Table 2) with NOE experiments [3, 4].

All the new diterpenoids found in *T. micropodioides* (**1**, **3**, **5**, **6** and **9**) exhibited the more common structural features of the neo-clerodane derivatives until now isolated from the *Teucrium* species [1].

EXPERIMENTAL

Mps are uncorr. Plant materials were collected in April 1986 near Greek Cape (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 powdered *Teucrium micropodioides* aerial parts (330 g) were extracted with Me_2CO (4 l) at room temp. for a week. The extract (19 g) was chromatographed on a silica gel column (Merck, No. 7734, deactivated with 15% H_2O, 500 g) eluted with *n*-hexane and *n*-hexane–EtOAc mixtures. Elution with EtOAc–*n*-hexane (3:2) yielded the following compounds in order of elution: 3-acetylteumicropin (**1**, 8 mg), teumicropodin (**6**, 500 mg), 3-deacetyl-20-*epi*-teulanigin (**9**, 46 mg), deacetylteupyrenone (**5**, 87 mg) and teumicropin (**3**, 32 mg).

3-Acetylteumicropin (**1**). Mp 256–259° (EtOAc–*n*-hexane); $[\alpha]_D^{20}$ +4.1° ($CHCl_3$; *c* 0.195); IR ν_{max}^{KBr} cm^{-1}: 3470, 3150, 3020, 2940, 1735, 1508, 1483, 1385, 1250, 1160, 1025, 998, 890, 880, 800; ^{1}H NMR (300 MHz, $CDCl_3$): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 404 $[M]^+$ (10), 344 (1), 329 (8), 267 (12), 185 (14), 173 (14), 145 (19), 105 (25), 95 (36), 94 (54), 91 (32), 81 (42), 77 (25), 55 (24), 43 (100). (Found: C, 65.20; H, 6.86. $C_{22}H_{28}O_7$ requires: C, 65.33: H, 6.98%).

Oxidation of 3-acetylteumicropin (**1**) *to give teupyrenone* (**2**). CrO_3–pyridine treatment of **1** (3 mg) for 24 hr at room temp. yielded a compound (2 mg), mp 214–216°, $[\alpha]_D^{20}$ −47.1° ($CHCl_3$; *c* 0.103), identical in all respects (IR, ^{1}H NMR, MS, mmp, TLC) with teupyrenone (**2**). Lit. [2] mp 213–215°, $[\alpha]_D^{18}$ −46.5°.

Teumicropin (**3**). Mp 195–198° (EtOAc–*n*-hexane); $[\alpha]_D^{22}$ −22.9° (pyridine; *c* 0.088); IR ν_{max}^{KBr} cm^{-1}: 3440, 3300, 3140, 3120, 2940, 1507, 1460, 1378, 1360, 1160, 1070, 1055, 1035, 997, 880, 875; ^{1}H NMR (300 MHz, $CDCl_3$ and pyridine-d_5): see Table 1; EIMS (70 eV, direct inlet) *m/z* (rel. int.): 362 $[M]^+$ (25), 344 (2), 329 (10), 298 (17), 267 (14), 220 (11), 185 (23), 145 (34), 105 (45), 95 (71), 94 (100), 91 (67), 81 (80), 77 (53), 55 (45), 41 (55). (Found: C, 66.39; H, 7.19. $C_{20}H_{26}O_6$ requires: C, 66.28; H, 7.23%.)

Diacetylteumicropin (**4**) *from 3-acetylteumicropin* (**1**) *and teumicropin* (**3**). Ac_2O–pyridine treatment of **1** (2 mg) and **3** (15 mg) 72 hr at room temp. quantitatively yielded the same derivative **4**: an amorphous powder which melted at 79–84°; $[\alpha]_D^{20}$ −24.5° ($CHCl_3$; *c* 0.110); IR ν_{max}^{KBr} cm^{-1}: 3140, 2950, 2890,

1735, 1505, 1455. 1375, t250, 1085, I025, 995, 890, 875: 'H NMR **(30t-) MHz, CDCI3):** see Table 1: ElMS (70 eV. direct inlet) m/z **(rel. int.): 446 [M] * 16), 386 (1), 326 12!, 249 (l 1), 185** (1 lk 145 **(t3),** 11)5 1131,95 (221, 94 142), 9l 1171,81 124i, 79 il0k 55 (111, 43 (101)i. **C>~H3oOs: M,** 446.

Deacetyheup),renone (51. Mp 235-240 ~EtOAc n-hexane): [:t]~2+1.6 (CHC13;cO.183);IR~'KSrcmmax ~: 3460, 3140, 3115, 3(R)5, 2941), 1712, 1500, 1460, 1345, 1275, 103tL 1015, 875, 795; ~tt NMR (300 MHz. CDCI3): see Table 1: ElMS 170 eV, direcl inlet) m;z (rel. int.l: 360 [M] 4 10.7). 342 111.4~.289 !2). 283 15), 2111 *(31,105(17),951171,94{1001,91* (131,81416), 77 t91, 5519). (Found: C. 66.59: H, 6.62. C2o1-1240(, requires: C 66.65: H, 6":I ['0.t

Teupyrenone (2)jrom compound 5. Ac20 pyridine treatment o~ 5 t15 rag) lot 24 hr at room temp. yielded teupyrenone 12, 14 mg after crystallization from EtOAc n-hexaneL mp 210 214 . [:~]~ - 48.8 (CHCI3 ; c//.26t), identical in all respects (IR, ~H N M R, MS, mmp, TLC} with the previously described ~ompound !see ref. [2] and above~.

7eumicropodin {6). Mp 238-241 (EtOAc n-hexane); [:~]D2 + 4) .v tCHCI3 ; c 0.303); IR l,KBrcm I : 3480, 3145. 3130, 3080, 3020, 2960, 2880, 1760, 1740 (br), t600, 1503. 1475, 1320. i230. 1178, 1040. 941i, 915, 875, 805, 790: ~H N MR i31Xl MHz, CDCI 3): see Table 1: ~3CNMR (75.4 MHz, CDC13 I: see Table 3: ElMS (70 eV, direct inlet)m,,z (tel. int): 462 [M] ~ 0,>.2), 402 [0.31, 342 (21, 324 (4), 312 14), 157 1131, 145 (121, 121 (17), 105 (15), 96 (46), 95 (60), 94 (23), 91 120t, 81 {391, 43 (100). (Found: (, 62.191 H. 6.51. C24H300 9 requires: C, 62.32: H, 6.541~o./

Compound 7. Ac20 pyridine treatment of teumicropodin (6, l(X)mg) for 72 hr at room temp. quantitatively yielded the derivative 7: an amorphous powder which melted at 116 121 : [:~]D2 + 5.1 CHCI~: c t).3951: IR ~KBrmaxcm i. 314(t. 3120, 3060, 2960, 2870, 1760. 1745 {br), 1505, 1390, 1365, i250. 1180. 1040. 1020, 875: ~H NMR (90 MHz. CDCI3): see Table I; ElMS (70 eV, direct *inlet)m/z* **(rel. int.j:** 504 [M] ~ (0.t). 444 !04~, ~72 (31, 312 **(16), 218 (7), 185 17), 157 (91, 96 (481.** 95 141). 94 **{l** *3),* ~! tI(}L 81 (22), 43 (I(X)). Cze,U320,o: M, 5(N

Oxidation oi teurnicropodin t6) *to ~lire compound 8.* CrO3 pyridine oxidation o1" 6 (50mg) in the usual manner yielded a substance 1411rag. after crystalliz,ation from EtOAc n-hexaneLmp192 194.[a]~-~+34.5 CHC'la:~I).3291, identicalin all respects (IR. ~H NMR, MS, mmp. IL1') v,ith the previously described compound 18, mp 189 190,5 ; [z~]-S ~ 36.6 {[7].

3-Deacetyi-20-epi-teulanigin (9) Mp 193 1'15 (FtOAc n-hexane): [~]~2 271 {CHCI,~: c 0. 148r }R 'KBrmaxc m l : 352(3140, 2950, 2870, 1745 (br). 17ILL I507. 1370. 125t), 1160. 1085. 1031/, 9L~d.8751 'l-.I NMR {200 MHz. CDCI3): see Table 1: ElMS t70 *eV,* direcl inlet) *m/=* (rd int.): [M] ~ absent, 41/2 [M - 60] ~ (1.5), 360 (61, 1329(41, 1311 171. 163 {10k 1t 1 (101,!15 124), 94 1371,91 1151, 81 i26!. 43 i{(R)). (Found: (', O2AI: 11. 648 C2,,H~:(),~ requires (, 62.32 H 6.541'.,l

20-epi-Teu]ani#in i101#',m ,'mng~(mnd 9 AC20 pyridine Ireat-merit o19 (lli rag) R)r 24 hr a! ro(!nl letup, quantila'ively yielded a compound, mp lt';I 183 {tK)Ac n-hexaneL [~]~ 51.8 1CttC13 c 02171. identical in ali respects {IR. ~tINMR, MS. romp. I-LC} v~ilh 2iwpt-tet ahem iliL mp 18,.2 18~ [s~l~ *52.1)Is]*

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