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Some Chemical Transformations of the *Neo*-Clerodane Diterpene Teubotrin[1]

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Abstract: *Starting from the natural* neo-*clerodane diterpenoid teubotrin* (**1**) *several* neo-*clerodane derivatives* (**3-7, 9-11**) *have been obtained. The naturally occurring diterpenoid teuscordinon* (**12**) *has also been synthesized from teubotrin* (**1**), *showing thereby how some of these transformations can be useful for the synthesis of other natural* neo-*clerodane diterpenes. The latter are of interest due to their activity as insect antifeedants and other important biological properties.*

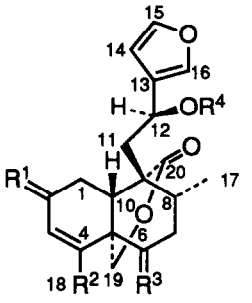
A large number of diterpenoids with the *neo*-clerodane skeleton have been isolated from plants in the last few years. Interest in these compounds has been stimulated by their biological activity as insect antifeedants and as antifungal, antitumour, antimicrobial and moluscicidal agents. The *Teucrium* species (family Labiatae) have afforded a great number of these compounds[3].

In continuation of our studies on *neo*-clerodane diterpenoids from *Teucrium* species[3], we were interested in establishing chemical correlations between some of these compounds[4] and also in obtaining synthetic derivatives in order to test biological activities[5]. This communication reports the results achieved by a series of reactions on the *neo*-clerodane diterpene teubotrin[6] (**1**, also named teulamifin B[6b]), previously isolated by us from *Teucrium botrys*[6a], *T. lamiifolium* and *T. polium*[6b]. These transformations allowed to obtain the derivatives **3-7** and **9-11** by selective acetylations, allylic oxidations and lactonization and translactonization reactions. Moreover, oxidation of the allylic C-18 methylene group of the C-18,C-19 cyclic ether moiety of compound **11** allowed the partial synthesis of teuscordinon (**12**), a natural *neo*-clerodan-3-en-18,19-olide derivative found in *T.*

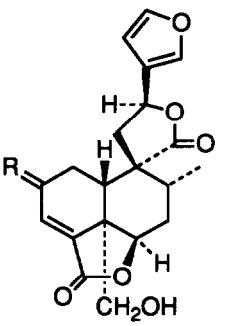
scordium[7]. The reactions reported herein provide suitable intermediates for the synthesis of other natural *neo*-clerodane diterpenoids and new substances for testing their biological activities, which is now in progress.

RESULTS AND DISCUSSION

In previous works[6] we reported the preparation of triacetylteubotrin (**2**) by acetic anhydride-pyridine treatment of the natural diterpenoid (**1**). Now, we have found that reaction of compound **1** with acetic anhydride-pyridine at room temperature for 48 hours gave triacetylteubotrin[6] (**2**, 61% yield) and a diacetyl derivative ($C_{24}H_{30}O_8$, 39% yield) for which structure **3** was established by comparing its ^1H and ^{13}C NMR spectroscopic data (see Tables 1 and 2, respectively) with those of triacetylteubotrin[6] (**2**). Moreover, chromium trioxide-pyridine oxidation of compound **3** yielded the keto derivative **4** ($C_{24}H_{28}O_8$, 72% yield) whose spectroscopic data (Tables 1 and 2, and Experimental) clearly revealed that it possessed a ketone at the C-6 position[3,4,7]. Since only compounds **2** and **3** were detected in this acetylation reaction, it is obvious that the C-12 and C-18 hydroxyl groups of teubotrin react more rapidly than the C-6β axial alcohol function, and this must be due to the steric hindrance showed by this last hydroxyl group.



	R^1	R^2	R^3	R^4
1	H_2	CH_2OH	αH,βOH	H
2	H_2	CH_2OAc	αH,βOAc	Ac
3	H_2	CH_2OAc	αH,βOH	Ac
4	H_2	CH_2OAc	O	Ac
5	H_2	CHO	αH,βOH	H
6	O	CHO	αH,βOH	H



7 R=O
8 R=H_2

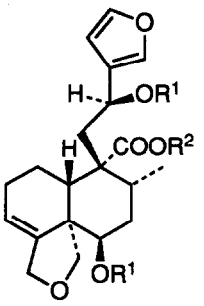
On the other hand, treatment of an acetone solution of teubotrin (**1**) with manganese dioxide yielded three compounds, **5**, **6** and **7**, in a 17.3:1.4:1 ratio, respectively. The major product was the aldehyde **5** ($C_{20}H_{24}O_6$, λ_{max} 220 nm, log ε 4.07; $\delta_{H\text{-}18}$ 9.51 s, $\delta_{C\text{-}18}$ 193.7 d), which underwent an additional oxidation of the allylic C-2 methylene group yielding the corresponding C-2 keto-derivative **6** ($C_{20}H_{22}O_7$, λ_{max} 214 and 233 nm, log ε 4.02 and 3.91, respectively; $\delta_{C\text{-}2}$ 197.5 s, $\delta_{C\text{-}18}$ 193.9 d, $\delta_{H\text{-}18}$ 9.56 s). The minor product of this reaction (**7**, $C_{20}H_{20}O_7$) showed ^1H and ^{13}C NMR spectra almost identical with those of teuscorodonin (**8**), a *neo*-clerodane diterpene previously isolated from *Teucrium scorodonia*[8]. In fact, the only differences between the ^1H and ^{13}C

Table 1. ^{1}H NMR Spectroscopic Data of Compounds **3-7** and **9-11**[a]

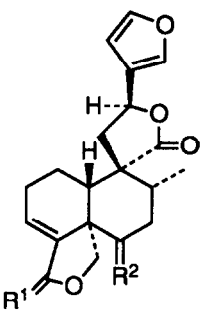
	3	**4**	**5**	**6**	**7**	**9**	**10**	**11**
H-1α	*b*	*b*	*b*	3.52 dd	2.94 dd	1.88 qd	1.39 qd	*b*
H-1β	*b*	*b*	*b*	3.54 dd	2.69 dd	*b*	*b*	*b*
H-3	5.98 br dd	6.00 br dd	6.94 dd	6.43 s	6.59 s	5.90 br d	5.79 br d	5.92 br dd
H-6α	4.08 t		4.86 t	4.81 t	5.15 dd	4.63 t	5.33 t	4.22 t
H-7α	1.64 ddd	*b*	1.68 ddd	1.66 ddd	1.89 ddd	*b*	2.40 ddd	*b*
H-7β	1.83 ddd	*b*	1.82 ddd	1.81 ddd	2.03 ddd	*b*	1.73 ddd	1.77 dt
H-8β	*b*	*b*	*b*	2.61 ddq	2.17 ddq	*b*	*b*	*b*
H-10β	*b*	*b*	2.73 dd	2.16 dd	2.53 dd	3.93 dd	2.67 dd	2.80 dd
H_A-11	2.35 dd	*b*	2.14 dd	1.97 dd	2.37 dd	2.38 dd	1.96 dd	2.43 dd
H_B-11	2.61 dd	2.72 dd	2.41 dd	2.41 dd	2.74 dd	3.22 dd	2.79 dd	2.50 dd
H-12	5.96 dd	5.86 dd	4.85 dd	4.83 dd	5.58 ddd	5.45 dd	6.08 dd	5.35 t
H-14	6.40 dd	6.42 dd	6.38 dd	6.32 dd	6.43 dd	6.72 dd	6.43 dd	6.41 dd
H-15	7.33 t	7.38 t	7.34 t	7.23 t	7.52 t	7.61 t	7.38 t	7.44 t
H-16	7.42 m	7.44 m	7.36 m	7.26 m	7.59 m	7.77 m	7.45 m	7.46 m
Me-17	0.80 d	0.97 d	0.83 d	0.78 d	1.12 d	1.37 d	1.09 d	1.02 d
H_A-18	4.47 d	4.72 br s	9.51 s	9.56 s		4.10 d	3.92 d	4.01 d
H_B-18	4.60 br d	4.72 br s				4.51 br dd	4.30 br dd	4.25 br dd
H_A-19	4.16 d	4.55 d	4.26 d	4.29 d	4.33 d	4.07 d	3.30 d	3.49 d
H_B-19	4.38 d	4.67 d	4.48 d	4.49 br d	4.46 d	4.45 d	3.72 d	4.17 d
OAc	2.03 s	2.03 s					2.07 s	
	1.98 s	1.98 s					2.02 s	
COOMe							3.60 s	
J								
1α,1β	*b*	*b*	*b*	19.3	17.9	12.1	12.2	*b*
1α,2α	*b*	*b*	*b*			4.3	4.2	*b*
1α,2β	*b*	*b*	*b*			12.1	12.2	*b*
1α,10β	*b*	*b*	13.1	16.9	13.5	12.2	12.5	13.1
1β,10β	*b*	*b*	1.8	4.6	4.6	1.6	1.5	1.8
3,2α	4.5	4.2	4.7			6.9	6.9	5.3
3,2β	2.2	2.1	2.7			<0.3	<0.3	3.0
3,18B	<0.3	<0.3	0	0		<0.3	<0.3	<0.3
6α,7α	2.7		2.7	2.7	6.2	2.8	2.9	3.5
6α,7β	2.7		2.7	2.7	11.6	2.8	2.9	3.5
7α,7β	14.7	*b*	14.5	14.6	13.4	*b*	14.9	14.3
7α,8β	12.6	*b*	12.9	12.9	4.8	*b*	12.3	*b*
7β,8β	4.3	*b*	4.2	4.1	3.3	*b*	3.7	3.5
8β,17	6.7	6.6	6.8	6.8	7.6	5.9	6.9	6.6
11A,11B	16.2	16.3	16.0	15.9	13.4	15.3	15.9	13.0
11A,12	9.6	9.3	10.1	10.4	3.2	2.2	3.0	8.7
11B,12	3.6	3.7	2.3	2.0	8.6	9.8	10.3	8.7
12,16	<0.3	<0.3	<0.3	<0.3	1.2	<0.3	<0.3	<0.3
14,15	1.8	1.7	1.7	1.8	1.8	1.7	1.8	1.7
14,16	0.6	0.6	0.9	0.8	0.8	0.8	0.9	0.7
15,16	1.8	1.7	1.7	1.8	1.8	1.7	1.8	1.7
18A,18B	12.4	0				10.6	9.5	9.4
18B,2α	0	0	0			4.0	4.0	3.0
19A,19B	12.5	13.2	12.4	12.5	11.1	8.0	8.1	9.1

[a]Chemical shifts are reported in δ values from internal TMS; *J* values in Hz. Spectral parameters were obtained by first order approximation. All these assignments have been confirmed by double resonance experiments. At 200 MHz (**3**, **4** and **11**) and 300 MHz (**5-7**, **9** and **10**). All in $CDCl_3$ solution except for **7** and **9** , both of them were recorded in pyridine-d_5 solution. [b]Overlapped signal.

NMR spectra of these compounds (Tables 1 and 2, and reference[8]) were consistent with the existence in the derivative **7** of a ketone at the C-2 position [λ_{max} 212 and 232 nm, log ε 4.20 and 4.11, respectively; ν_{CO} 1695 cm^{-1} (α,β-unsaturated ketone); δ_{C-1} 36.0 t, δ_{C-2} 198.4 s, δ_{C-3} 127.8 d, δ_{C-4} 156.4 s] instead of the C-2 methylene group of teuscorodonin (**8**: $C_{20}H_{22}O_6$, λ_{max} 216 and 220 nm, log ε 3.95 and 4.00; δ_{C-1} 17.6 t, δ_{C-2} 24.6 t, δ_{C-3} 134.9 d, δ_{C-4} 139.7 s)[8]. In particular, the presence in compound **7** of a C-20,C-12 γ-lactone structural moiety was clearly evidenced by its IR absorption at 1765 cm^{-1} and the chemical shifts of the C-12 and C-20 carbon atoms at δ 72.4 d and 177.1 s, respectively, typical of γ-lactones[3,4,6-8], but very different from the values observed for the C-20,C-19 δ-lactone regioisomers[4,6] (δ_{C-12} 63-65 and δ_{C-20} 170-173 ppm; see also Table 2, compounds **3**-**6**). Compound **7** must be generated from the derivative **6** by initial formation of a C-18,C-6β hemiacetal, which was oxidised to the corresponding C-18,C-6β γ-lactone, and a translactonization reaction from the C-20,C-19 δ-lactone to the C-20,C-12 γ-lactone isomer, possibly forced by the closure of the C-18,C-6β hemiacetal or lactone bridge.



	R^1	R^2
9	H	H
10	Ac	Me



	R^1	R^2
11	H_2	αH,βOH
12	O	O

When a methanolic solution of teubotrin (**1**) was treated with an aqueous solution of NaOH compound **9** was formed in moderate yield (69%). The structure of this substance (**9**) was firmly supported by its spectroscopic data and by those of its derivative **10**, obtained by successive treatment of **9** with diazomethane and acetic anhydride-pyridine (see Tables 1 and 2, and Experimental). In particular, the existence of an ether bridge between the C-18 and C-19 positions of compounds **9** and **10** was evidenced by the absence of hydroxyl absorptions in the IR spectrum of **10**, the observed downfield shift of the C-6α and C-12 protons of compound **10** with respect to **9** (Δδ +0.70 and +0.63 ppm, respectively) and the minor J_{gem} values of the C-18 and C-19 methylene protons showed by these compounds ($J_{18A,18B}$=10.6 and 9.5 Hz, and $J_{19A,19B}$= 8.0 and 8.1 Hz in **9** and **10**, respectively) with respect to those reported[6] for some *neo*-clerodane derivatives having hydroxymethylene or acetoxymethylene groups at the C-18 and C-19 positions ($J_{18A,18B}$=11.3-12.6 Hz, $J_{19A,19B}$=11.1-12.8 Hz).

It is surprising to obtain a compound such as **9** from the reaction of teubotrin (**1**) with alkali, but its formation may be rationalized considering that the hydrolysis of the C-20,C-19 δ-lactone occurs via an alkyl-oxygen cleavage[9] originating a C-19 cation, which reacts with the C-18 hydroxyl group forming the C-18,C-19 ether bridge of the derivative **9**.

Table 2. ^{13}C NMR Data of Compounds 3-7, 10 and 11[a]

C	3	4	5	6	7	10	11
1	19.9 t[b]	20.4 t	19.7 t	35.8 t	36.0 t	21.4 t	20.9 t
2	25.3 t	25.0 t	27.0 t	197.5 s	198.4 s	26.9 t	27.6 t
3	133.8 d	130.6 d	156.5 d	141.1 d	127.8 d	125.6 d	126.7 d
4	134.2 s	132.8 s	143.2 s	156.0 s	156.4 s	140.6 s	140.7 s
5	41.3 s	51.0 s	41.0 s	42.0 s	45.3 s	50.5 s*	50.8 s*
6	69.5 d	207.9 s	68.1 d	67.9 d	78.9 d	70.2 d	67.7 d
7	36.7 t	46.1 t	36.9 t*	37.5 t*	31.1 t	36.9 t	34.0 t
8	30.4 d	39.4 d	30.8 d	30.5 d	37.4 d	31.7 d	33.5 d
9	49.6 s	49.3 s	49.6 s	50.1 s	48.4 s	49.9 s*	50.7 s*
10	36.0 d	45.7 d	36.6 d	37.1 d	46.8 d	41.9 d	43.6 d
11	33.1 t	33.2 t	36.1 t*	37.2 t*	43.5 t	32.6 t	42.1 t
12	64.6 d	64.1 d	63.0 d	63.2 d	72.4 d	65.0 d	71.5 d
13	125.7 s	125.3 s	130.3 s	129.9 s	126.8 s	125.7 s	125.1 s
14	108.7 d	108.5 d	108.4 d	108.2 d	108.9 d	108.6 d	108.1 d
15	143.3 d	143.6 d	143.4 d	143.8 d	145.0 d	143.4 d	144.1 d
16	140.0 d	140.2 d	138.4 d	138.6 d	139.9 d	140.0 d	139.6 d
17	16.2 q	16.9 q	16.2 q	16.1 q	17.7 q	16.1 q	16.3 q
18	66.0 t	65.7 t	193.7 d	193.9 d	168.7 s	68.8 t[#]	66.1 t
19	74.1 t	71.5 t	72.9 t	71.5 t	66.1 t	67.2 t[#]	70.7 t
20	171.9 s	170.5 s	172.4 s	170.9 s	177.1 s	174.5 s	177.0 s
OAc	170.2 s	170.2 s				170.0 s	
	170.0 s	169.8 s				169.8 s	
	21.3 q	21.3 q				21.5 q	
	21.0 q	21.1 q				21.1 q	
COOMe						51.1 q	

[a]Chemical shifts are reported in δ values from internal TMS. At 50.3 MHz, all in $CDCl_3$ solution except for 7, which was recorded in pyridine-d_5 solution. [b]Multiplicities were determined by DEPT pulse sequences. *,#These assignments may be reversed.

Finally, treatment of compound 9 with a dehydrating reagent (P_2O_5, see Experimental) gave the C-20,C-12 γ-lactone derivative 11 (84% yield), which was transformed into teuscordinon[7] (12, 23% yield) by oxidation of both C-6β hydroxyl and C-18 methylene (allylic and ethereal) groups by using chromium trioxide in dry pyridine and methylene chloride solution[10].

EXPERIMENTAL SECTION

Melting points are uncorrected. Starting material (1, teubotrin) was available from previous studies[6].

Triacetylteubotrin (2) *and 12,18-diacetylteubotrin* (3) *from teubotrin* (1). Teubotrin (1, 500 mg) was treated with a mixture of Ac_2O (8 ml) and pyridine (2.5 ml) at room temperature for 48 h. Work-up in the usual manner gave a residue (550 mg), which was subjected to column chromatography [silica gel Merck No. 7734, deactivated with 15% H_2O (w/v), 14 g; petrol-EtOAc 3:7 as eluent] yielding triacetylteubotrin (2, 300 mg, less polar constituent, identical with the previously described compound[6]) and 12,18-diacetylteubotrin (3, 190 mg): mp 129-133°C (amorphous solid); $[\alpha]_D^{16}$ -56.5° ($CHCl_3$, *c* 0.407). IR (KBr) ν_{max} cm^{-1}: 3510, 3460, (OH);

3150, 3130, 1505, 870 (furan); 1720, 1715, 1240 (OAc); 1740 (δ-lactone). ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (70 eV, direct inlet) *m/z* (rel. int.): $[M]^+$ absent, 404 $[M-C_2H_2O]^+$ (9), 386 (23), 215 (4), 197 (5), 187 (5), 171 (12), 143 (10), 105 (21), 97 (17), 95 (22), 91 (33), 81 (26), 43 (100). (Found: C, 64.49; H, 6.52. $C_{24}H_{30}O_8$ requires: C, 64.56; H, 6.77%).

Chromium trioxide-pyridine oxidation of compound **3** *to give derivative* **4**. CrO_3-pyridine oxidation of **3** (70 mg) in the usual manner yielded **4** (50 mg, after crystallization from EtOAc - *n*-hexane): mp 164-168 °C; $[\alpha]_D^{16}$ -129.7° ($CHCl_3$, *c* 0.148). IR (KBr) ν_{max} cm^{-1}: 3140, 1500, 875 (furan); 1740 (δ-lactone); 1730, 1720, 1250, 1240 (OAc); 1715 (ketone). ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (70 eV, direct inlet) *m/z* (rel. int.): $[M]^+$ absent, 402 $[M-C_2H_2O]^+$ (26), 384 (25), 342 (23), 300 (18), 187 (13), 133 (10), 105 (17), 95 (25), 91 (23), 69 (19), 43 (100). (Found: C, 64.75; H, 6.60. $C_{24}H_{28}O_8$ requires: C, 64.85; H, 6.35%).

Oxidation of teubotrin (**1**) *with manganese dioxide*: *Compounds* **5**, **6** *and* **7**. To a solution of **1** (340 mg) in dry Me_2CO (250 ml) MnO_2 (12 g) was added, and the reaction mixture was stirred at room temperature for 4 h. Then, *n*-hexane (200 ml) was added and the reaction mixture filtered through a celite pad and the solvents evaporated leaving a residue (318 mg), which was chromatographed on a silica gel column (10 g) eluted with petrol - EtOAc mixtures, yielding the following compounds in order of increasing chromatographic polarity: **5** (207 mg), **6** (17 mg) and **7** (12 mg).

Compound **5**. Amorphous solid, mp 85-90 °C; $[\alpha]_D^{16}$ -69.6° ($CHCl_3$, *c* 0.181). IR (KBr) ν_{max} cm^{-1}: 3430 (OH); 3140, 1505, 875 (furan); 1710 (δ-lactone); 1680, 1635 (α,β-unsaturated aldehyde). UV (MeOH) λ_{max} nm (log ε): 220 (4.07). ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (70 eV, direct inlet) *m/z* (rel. int.): 360 $[M]^+$ (39), 342 (37), 312 (13), 217 (12), 185 (22), 143 (24), 128 (29), 111 (36), 97 (39), 95 (100), 91 (59), 81 (60). (Found: C, 66.49; H, 6.54. $C_{20}H_{24}O_6$ requires: C, 66.65; H, 6.71%).

Compound **6**. Mp 138-140 °C (EtOAc - *n*-hexane); $[\alpha]_D^{24}$ +32.2 ° ($CHCl_3$, *c* 0.146). IR (KBr) ν_{max} cm^{-1}: 3440 (OH); 3140, 1505, 875 (furan); 1740 (δ-lactone); 1690 br (α,β-unsaturated aldehyde and ketone). UV (MeOH) λ_{max} nm (log ε): 214 (4.02), 233 sh (3.91). ^{1}H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (70 eV, direct inlet) *m/z* (rel. int.): 374 $[M]^+$ (7), 356 (5), 344 (22), 326 (15), 199 (29), 178 (21), 148 (30), 115 (25), 97 (30), 95 (100), 91 (50), 81 (64), 77 (40), 41 (42). (Found: C, 63.97; H, 5.81. $C_{20}H_{22}O_7$ requires: C, 64.16; H, 5.92%).

Compound **7**. Mp 220-222 °C (EtOAc - *n*-hexane); $[\alpha]_D^{24}$ -12.7° ($CHCl_3$-MeOH 9:1, *c* 0.165). IR (KBr) ν_{max} cm^{-1}: 3570, 3520 (OH); 3140, 3120, 1505, 875 (furan); 1765 (γ-lactone); 1745 (α,β-unsaturated γ-lactone); 1695 (α,β-unsaturated ketone). UV (MeOH) λ_{max} nm (log ε): 212 (4.20), 232 sh (4.11). (Found: C, 64.61; H, 5.52. $C_{20}H_{20}O_7$ requires: C, 64.51; H, 5.41%).

Compound **9** *from teubotrin* (**1**). Compound **1** (520 mg) was dissolved in MeOH (30 ml) and an aqueous solution of NaOH (10%, w/v, 200 ml) was added and the reaction mixture heated at 105 °C for 7 h. Then, the reaction mixture was cooled and washed four times with $CHCl_3$. The alkaline solution was then acidified

(pH~6) with aqueous 5 % H_2SO_4 and extracted with $CHCl_3$ (4x25 ml). The extract was washed with H_2O, dried over Na_2SO_4 and the solvent evaporated yielding a residue (270 mg) from which the derivative **9** (240 mg) was obtained by crystallization from MeOH-Et_2O: mp 204-207 °C; $[\alpha]_D^{20}$ -163.9° ($CHCl_3$, *c* 0.113). IR (KBr) ν_{max} cm^{-1}: 3000-2500 br, 1690 (COOH); 3420 (OH); 3140, 1505, 880 (furan). ^1H NMR: Table 1. EIMS (70 eV, direct inlet) *m/z* (rel. int.): 362 $[M]^+$ (21), 344 (7), 314 (99), 296 (23), 220 (32), 187 (47), 157 (40), 119 (61), 118 (62), 95 (100), 91 (70), 81 (47). (Found: C, 66.01; H, 7.53. $C_{20}H_{26}O_6$ requires: C, 66.28; H, 7.23%).

Derivative **10** *from compound* **9**. The acid **9** (150 mg), dissolved in Et_2O (250 ml) plus MeOH (2 ml), was treated with an excess of an ethereal solution of CH_2N_2. Work-up in the usual manner gave a residue which, without characterization, was treated with Ac_2O-pyridine at room temperature for 48 h. yielding the derivative **10** (175 mg, after crystallization from EtOAc - *n*-hexane): mp 205-208 °C; $[\alpha]_D^{20}$ -96.5° ($CHCl_3$, *c* 0.228). IR (KBr) ν_{max} cm^{-1}: 3110, 1505, 875 (furan); 1740, 1730 br, 1250 (COOMe and OAc). ^1H NMR: Table 1. ^{13}C NMR: Table 2. EIMS (70 eV, direct inlet) *m/z* (rel. int.): 460 $[M]^+$ (10), 400 (3), 340 (12), 281 (22), 250 (46), 246 (50), 214 (26), 187 (32), 169 (31), 157 (54), 95 (49), 91 (30), 43 (100). (Found: C, 64.99; H, 7.30. $C_{25}H_{32}O_8$ requires: C, 65.22; H, 7.00%).

Lactone **11** *from hydroxy acid* **9**. To a solution of compound **9** (120 mg) in dry THF (5 ml) and dry CH_2Cl_2 (40 ml) P_2O_5 (300 mg) was added and the reaction mixture was stirred at room temperature for 3.5 h. After decantation of a gelatinous precipitate, the organic solution was washed with H_2O, dried (Na_2SO_4) and evaporated giving a residue (100 mg). This residue was purified by column chromatography (silica gel, *n*-hexane-EtOAc 3:1 as eluent) yielding 96 mg of compound **11** as an amorphous solid, mp 94-98 °C; $[\alpha]_D^{20}$ -114.6° ($CHCl_3$, *c* 0.114). IR (KBr) ν_{max} cm^{-1}: 3420 (OH); 3140, 1505, 875 (furan); 1760 (γ-lactone). ^1H NMR : Table 1. ^{13}C NMR: Table 2. EIMS (70 eV, direct inlet) *m/z* (rel. int.): $[M]^+$ absent, 314 $[M\text{-}CH_2O]^+$ (24), 296 (2), 220 (8), 205 (6), 187 (15), 157 (15), 118 (34), 105 (28), 95 (80), 91 (61), 81 (57), 43 (87), 41 (100). (Found: C, 69.50; H, 7.27. $C_{20}H_{24}O_5$ requires: C, 69.75; H, 7.02%).

Teuscordinon[7] (**12**) *from compound* **11**. To a mixture of dry pyridine (0.8 ml) and dry CH_2Cl_2 (10 ml) was added CrO_3 (1.5 g) at 0 °C. After 0.5 h., 42 mg of compound **11** in dry CH_2Cl_2 (2 ml) were added and the reaction mixture was refluxed for 50 h. Work-up in the usual manner gave a residue (30 mg), from which 10 mg of a compound [mp 235-236 °C (Me_2CO-Et_2O); $[\alpha]_D^{20}$ -94.0° (dioxane, *c* 0.133)] were isolated by column chromatography (silica gel, *n*-hexane-EtOAc 4:1 as eluent). This substance was identical in all respects [mp, ^1H NMR (300 MHz, $CDCl_3$), IR, MS] with teuscordinon [**12**, mp 235 °C (Et_2O-Me_2CO); $[\alpha]_D^{24}$ -84.1° (dioxane, *c* 1.2)][7]. Comparison (mmp, TLC) with an authentic sample[7] confirmed the identity.

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