Abietane and Rearranged Abietane Diterpenes from *Salvia montbretii*

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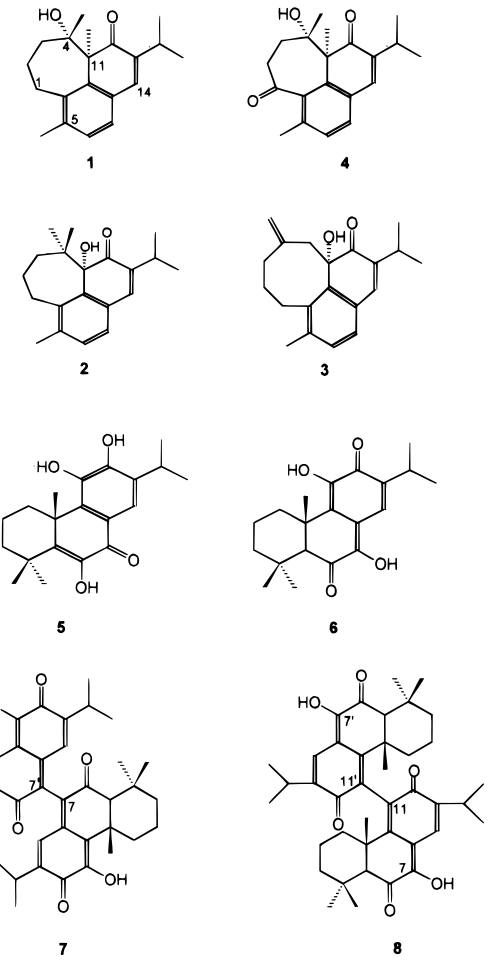
Received February 1, 1996[⊗]

From the roots of *Salvia montbretii* six new diterpenoids were isolated in addition to eleven known compounds. The new compounds were established as salvibretol (**1**), 1-oxosalvibretol (**4**), 6-hydroxysalvinolone (**5**), 7-hydroxytaxodione (**6**), 7,7′-bistaxodione (**7**), and 11,11′-didehydroxy-7,7′-dihydroxytaxodione (**8**), using 1D and 2D NMR techniques.

In previous studies on the roots and aerial parts of *Salvia montbretii* Benth. (Lamiaceae) we have reported the isolation of the diterpenes demethylcryptojaponol, ferruginol, ferruginyl 12-methyl ether, 14-hydroxyferruginol, hypargenin F, salvinolonyl 12-methylether, and taxodione;[1,2] the triterpenes α-amyrin, lupeol, monogynol A, and its 3*β*-*cis*- and *trans*-coumaryl esters; oleanolic and ursolic acids; the sterol sitosterol; and the flavonoids apigenin, luteolin, and cirsiliol.[3] In the present study on a new collection of the roots we have obtained six new diterpenoids (**1, 4**−**8**) constituted by two abietanes (**5, 6**), two rearranged abietanes (**1, 4**), and two dimeric compounds (**7, 8**). The known compounds were microstegiol,[4] saprorthoquinone, salvinolone,[5] candidissiol,[6] 11-hydroxy-12-methoxy-8,11,13-abietatriene,[7] 1-oxoaethiopinone,[8] salvicanaric acid,[9] limbinol, salvilimbinol,[10] taxodione,[11] and ferruginol.[12]



Results and Discussion

The EIMS of the first new compound, salvibretol (**1**), showed a molecular ion peak at *m*/*z* 298 analyzing for $C_{20}H_{26}O_2$, and HRCIMS gave a $[M + 1]^+$ peak at *m*/*z* 299.1988, thereby verifying the molecular formula. The ^{13}C-NMR spectrum was consistent with a diterpene structure in which the 20 carbon atoms consisted of five methyl quartets, three methylene triplets, four methine doublets, and eight quaternary singlets. One of the quarternary carbons that was hydroxylated appeared at *δ* 85.0, and another occurred at *δ* 202.9 and was attributed to an enone carbonyl. The IR spectrum of **1** supported the presence of a tertiary hydroxyl group showing a sharp peak at 3450 cm^{-1}, a conjugated oxo group at 1700 cm^{-1}, as well as aromaticity and unsaturation peaks at 1500, 1565, 1600, and 1620 cm^{-1}. The ^{1}H-NMR spectrum of **1** showed the presence of an isopropyl group, with signals at *δ* 1.31 and 1.35 (each 3H, d, *J* = 7 Hz, H-16 and H-17) and a methine septet at *δ* 3.35 (1H, *J* = 7 Hz, H-15). Two methyl singlets were at *δ* 1.15 and 1.62 for H-18 and H-19, and another methyl singlet was observed at *δ* 2.42 for H-20. A diagnostic signal occurred at *δ* 3.83 (1H, ddd, *J* = 15.0, 13.0, 5.0 Hz), being typical for H-1*β* and indicative of a rearranged abietane diterpene similar to analogous signals from microstegiol (**2**) and candidissiol (**3**), previously isolated from *Salvia microstegia*[4] and *Salvia candidissima*.[6] Downfield signals for **1** were at *δ* 7.48 (1H, d, *J* = 8.8 Hz, H-7), 7.33 (1H, s, H-14) 7.08 (1H, d, *J* = 8.8 Hz, H-6), and 6.33 (1H, br s, D_2O exchangeable, C-4 OH). The HETCOR NMR experiment showed direct correlations between protons and carbons for **1** (Table 1). Although it has a structural similarity to microstegiol (**2**), compound **1** exhibited some chemical-shift differences, especially with one of the methyl singlets resonating at *δ* 1.62. It was apparent that the C-4 methyl and the C-11 hydroxy groups of **2** were interchanged in **1**. The possible mechanism of this rearrangement was considered from microstegiol (**2**) as shown in Scheme 1. In order to assign the placement of the groups unambiguously in **1**, an extensive selective INEPT experiment was carried out. Irradiation of H-15 (*δ* 3.35) enhanced C-14 (*δ* 120.7), C-16 (*δ* 22.3), and C-12 (*δ* 202.9). Irradiation of Me-18 (*δ* 1.15) enhanced C-4 (*δ* 85.0) and C-19 (*δ* 27.4), while irradiation of Me-19 (*δ*

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⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1996.

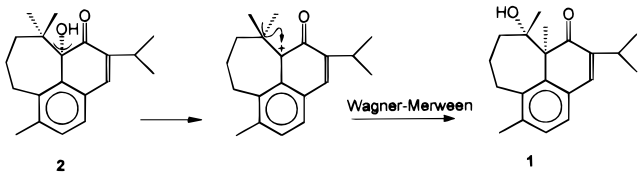
S0163-3864(96)00222-4 CCC: $12.00

Table 1. ^{1}H- and ^{13}C-NMR Data of Compounds 1, 4, and 5

	1[a]		**4**[b]		**5**[c]	
position	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	3.83 ddd, 3.02 ddd	26.5 t		210.8 s	3.0 ddd, 1.50 m	36.6 t
2	2.20 ddd, 1.72 m	23.0 t	2.19 ddd, 1.65 dt	41.2 t	2.0 m, 1.30 m	17.9 t
3	1.60 ddd, 1.20 m	33.3 t	3.04 ddd, 2.67 dt	35.1 t	1.90 ddd, 1.68 m	30.4 t
4		85.0 s		84.3 s		37.6 s
5		132.7 s		132.2 s		170.8 s
6	7.08 d	126.7 d	7.11 d	126.3 d		141.0 s
7	7.48 d	125.8 d	7.62 d	128.1 s		180.0 s
8		134.1 s		126.8 s		123.2 s
9		129.7 s		130.4 s		132.9 s
10		147.3 s		147.4 s		38.3 s
11		41.6 s		41.2 s		143.4 s
12		202.9 s		202.3 s		145.6 s
13		134.9 s		136.6 s		138.3 s
14	7.33 s	120.7 d	7.41 s	121.1 d	7.72 s	116.6 d
15	3.35 sept	27.6 d	3.35 sept	27.8 d	3.05 sept	27.4 d
16	1.31 d	22.3 q	1.28 d	22.3 q	1.28 d	22.4 q
17	1.35 d	22.4 q	1.33 d	22.3 q	1.32 d	22.4 q
18	1.15 s	26.3 q	1.22 s	25.9 q	1.42 s	22.6 q
19	1.62 s	27.4 q	1.67 s	26.2 q	1.43 s	28.0 q
20	2.42 s	19.1 q	2.32 s	18.7 q	1.67 s	27.9 q

[a] J (Hz) **1**: 1α,1β = 13; 1α,2α = 2.5; 1α,2β = 5.5; 1β,2α = 15; 1β,2β = 5; 2α,2β = 14; 2α,3α = 3; 2α,3β = 16; 3α,3β = 13. [b] J (Hz) **4**: 2α,2β = 14.5; 2α,3α = 2β,3β = 3.5; 2α,3β = 16; 3α,3β = 15. [c] J (Hz) **5**: 1α,1β = 13; 1α,2α = 1β,2α = 3; 2α,2β = 14.

Scheme 1. Formation of salvibretol from microstegiol



1.62) enhanced C-4 (δ 85.0) and C-18 (δ 26.3); other enhancements are in agreement with the given structure of compound **1**.

The HREIMS of the second compound, 1-oxosalvibretol (**4**), indicated a molecular formula of $C_{20}H_{24}O_3$ (*m/z* 312.1744). The ^{13}C-NMR spectrum (Table 1) displayed the presence of a diterpenoid structure consisting of four methyl quartets for five methyl groups, two methylene triplets, four methine doublets, and nine quarternary singlets. The ^{1}H-NMR spectrum of **4** showed similarities to that of compound **1**. The presence of an isopropyl group followed from the methyl doublets at δ 1.28 and 1.33 (each 3H, J = 7 Hz, H-16 and H-17) and a methine septet at δ 3.35 (1H, J = 7 Hz, H-15). Three methyl singlets were at δ 1.22 (H-18), 1.67 (H-19), and 2.32 (H-20). Other signals were at δ 3.04 (1H, ddd, J = 3.5, 15.0, 16.0 Hz, H-3β), 5.96 (C-4 OH, D_2O exchangeable), 7.11 (1H, d, J = 8.5 Hz, H-6), 7.41 (1H, s, H-14), 7.62 (1H, d, J = 8.5 Hz, H-7). When compared to compound **1**, an additional oxo group was observed at δ 210.8 in the ^{13}C-NMR spectrum of **4**, which could only be placed at C-1 due to the lack of H-1β at δ 3.83, which was as confirmed by the SINEPT experiment. The HETCOR experiment showed the direct correlations between the carbons and protons (Table 1). In the SINEPT experiment, when H-3β (δ 3.04) was irradiated, C-1 (δ 210.8) was enhanced; when H-3α (δ 2.67) was irradiated C-1 (δ 210.8), C-2 (δ 35.1), and C-4 (δ 84.3) were enhanced; irradiation of Me-19 (δ 1.67) enhanced C-4 (δ 84.3) and C-18 (δ 25.9), and irradiation of Me-18 (δ 1.22) enhanced C-4 and C-19 (δ 26.2). Irradiation of H-15 (δ 3.35) enhanced C-12 (δ 202.3) and C-14 (δ 121.1), and irradiation of H-14 (δ 7.41) enhanced C-8 (δ 126.8), C-10 (δ 147.4), C-12 (δ 202.3), and C-15 (δ 27.8). The rest of the signals are in agreement with the structure given for **4**.

The EIMS of 6-hydroxysalvinolone (**5**) indicated a molecular formula $C_{20}H_{26}O_4$ (*m/z* 330), and the HRCIMS (*m/z* 331.1906) confirmed this information. The ^{13}C-NMR spectrum of **5** displayed the presence of four methyl quartets for five methyl groups, three methylene triplets, two methine doublets, and ten quarternary carbon atoms. The ^{1}H-NMR spectrum indicated an abietane structure from signals at δ 3.05 (1H, septet, J = 7 Hz, H-15), 1.28, and 1.32 (each 3H, d, J = 7 Hz, H-16 and H-17) and three methyl singlets—one at δ 1.67 (H-20), two others at δ 1.42 and 1.43 (H-18 and H-19)—all indicative of a double bond and a hydroxyl group at C-6 as observed in similar compounds.[13] The only downfield proton was at δ 7.72 (1H, s, H-14), which suggested the presence of a carbonyl group at C-7. The signal at δ 3.00 (1H, br dd, J = 13.0, 3.2 Hz, H-1β) indicated a hydroxyl group at C-11.[14] Acetylation of **5** yielded the acetyl derivative (**5a**) having three acetyl signals at δ 2.37 (6H, s, 2 × OAc) and 2.32 (3H, s, OAc). After acetylation, the two methyl groups at C-4 were shifted upfield to δ 1.23 and 1.27, thus indicating that the effect of C-6 hydroxylation on the C-4 methyl groups had disappeared, while the proton signal at C-14 moved to δ 8.12 showing a more pronounced carbonyl effect on the proton at C-14. The ^{13}C-NMR signals (Table 1) correlated with the proposed structure for compound **5**.

The spectral data of compound **6** were quite similar to those of taxodione,[11] with the only difference being the presence of one more hydroxyl group. The HREIMS indicated a molecular formula of $C_{20}H_{26}O_4$ (*m/z* 330.1822). The ^{1}H-NMR spectrum displayed three methyl singlets at δ 1.32, 1.28, and 1.10, indicating the presence of three methyl groups at C-18, C-19, and C-20 and two methyl doublets at δ 0.95 and 0.85 (each 3H, d, J = 7 Hz, H_3-16 and H_3-17), together with a methine signal at δ 2.92 (1H, d of septet, J = 1, 7 Hz, H-15), showing the presence of an isopropyl group. Downfield signals were observed at δ 6.45 (1H, d, J = 1.5 Hz, H-14) and 7.65 (1H, s, D_2O exchangeable, C-11 OH). These two signals were typical for the C-ring of taxodione, but the signal

Table 2. ^{13}C-NMR Data of Compounds 6 and 8

carbon	6	8
1	42.3 t	42.3 t
2	18.7 t	18.6 t
3	36.7 t	36.7 t
4	32.9 s	33.5 s
5	62.2 d	62.1 d
6	182.0 s[a]	181.1 s
7	142.3 s[b]	141.0 s
8	126.5 s	126.7 s
9	141.9 s	145.5 s
10	41.8 s	41.7 s
11	145.4 s[b]	136.8 s
12	183.4 s[a]	200.4 s
13	138.4 s	144.8 s
14	133.1 d	133.1 d
15	26.9 d	27.0 d
16	21.4 q	21.4 q[c]
17	21.4 q	21.2 q[c]
18	32.5 q	32.8 q
19	21.8 q	21.5 q
20	21.0 q	21.0 q

[a−c] Exchangeable assignments.

at δ 5.77 (H-7) present in taxodione was not observed in compound **6**, and instead there was a signal at δ 7.22 (1H, s, D_2O exchangeable) consistent with the presence of a second hydroxyl group at C-7. Because there was no proton geminal to the second hydroxyl group, it could not be placed at C-1−C-3, which exhibited three aliphatic methylene triplets in the ^{13}C-NMR spectrum (Table 2). The only possible carbons for the second hydroxyl group were either at C-7 or C-14. Because the proton at δ 6.45 is a doublet that coupled with H-15 from spin-decoupling experiments, the second hydroxyl group was placed at C-7. The appearance of a singlet signal at δ 2.90 (H-5) was also indicative of a taxodione structure. The ^{13}C-NMR spectrum of **6** displayed four methyl quartets for five methyl groups, three methylene triplets, three methine doublets, and nine quarternary carbon singlets (Table 2). The given data indicated that compound **6** is 7-hydroxytaxodione.

The HREIMS of compound **7** showed a molecular formula of $C_{40}H_{50}O_6$ (*m/z* 626.3720). The ^{1}H NMR spectrum of **7** resembled those of taxodione and 7-hydroxytaxodione, with methyl singlets at δ 1.41, 1.24, and 1.05, corresponding to H_3-18, H_3-19, and H_3-20; two methyl doublets at δ 1.08 and 1.10 (each 3H, d, J = 7 Hz, H-16 and H-17); and a methine proton at δ 2.98 (1H, d septet, J = 1.2, 7 Hz, H-15); H-5 was at δ 2.71, occurring as a sharp singlet. There were only two downfield signals at δ 6.60 (1H, d, J = 1.2 Hz, H-14) and 7.63 (1H, s, C-11 OH, D_2O exchangeable). The presence of a fragment peak at *m/z* 313 in its mass spectrum assignable to half of the structure indicated that the compound could be a dimeric taxodione. In case of a symmetrical dimer the linkages of two taxodione molecules could be either at C-14, C-11, C-7 or, if the compound is asymmetric, the conjunction could be between C-7−C-14, C-11−C-7, or C-11−C-14. In the ^{1}H-NMR spectrum of **7**, the signals indicated a symmetrical dimer, otherwise more signals should have been observed for the olefinic protons. In the ^{1}H-NMR spectrum, the H-11 and H-14 signals were clearly seen as in taxodione, so the only plausible place for two units to join together was C-7−C-7′. The spectral data indicated that compound **7** is 7,7′-bistaxodione.

The final new compound, **8**, was also dimeric, and its spectral data were quite similar to those of **7**. Only the carbons, when the monomeric units were linked in compound **8**, were found to be different from those in **7**. The HREIMS of **8** indicated a molecular formula of $C_{40}H_{50}O_6$ (*m/z* 626.3722). The ^{1}H-NMR spectrum showed methyl signals at δ 1.02, 1.20, and 1.26 (each 3H, s) for H_3-18, H_3-19, and H_3-20. Two other methyl signals were at δ 0.78 and 0.88 (each 3H, d, J = 7 Hz, H_3-16 and H_3-17), and a methine doublet of septets at δ 2.96 (1H, J = 1.2, 7 Hz, H-15) as well as a singlet at δ 2.92 (1H, s, H-5) were also observed. Downfield signals were observed at δ 6.37 (1H, d, J = 1.2 Hz, H-14) and 7.18 (1H, s, D_2O exchangeable, C-7 OH), which was quite similar to compound **6**. All ^{1}H- and ^{13}C-NMR spectral data of compound **8** indicated a symmetrical dimeric compound, with the presence of a C-7 hydroxyl group (at δ_H 7.18; δ_C 141.0) as well as a H-14 signal (δ_H 6.37; δ_C 133.1), so that the two parts of the molecule were joined together at C-11−C-11′ to form 11,11′-didehydroxy-7,7′-dihydroxytaxodione.

Experimental Section

General Experimental Procedures. The spectra were recorded with the following instruments: IR, Perkin-Elmer 983; UV, Varian-Techtron 635; ^{1}H and ^{13}C NMR, Bruker AC 200L; SINEPT experiments were recorded on a Bruker 300 MHz instrument; HRMS, VG ZabSpec.

Plant Material. The roots of *S. montbretii* were collected from southeastern Turkey (Güreniz-Nizip, Gaziantep) in July 1993. A voucher specimen is deposited in the Herbarium of Faculty of Pharmacy, University of Ankara, AEF 17915.

Extraction and Isolation. The dried and roughly powdered roots of the plant (1.7 kg) were extracted with Me_2CO at room temperature. After evaporation of the solvent, 42 g of a residue were obtained and fractioned on a Si gel column (5 × 70 cm) eluting with petroleum ether, followed by a gradient of CH_2Cl_2 up to 100%, and finally by MeOH. The following compounds were isolated in succession: microstegiol (**2**) (25 mg), salvibretol (**1**) (25 mg), saprorthoquinone (12 mg), salvinolone (27 mg), 6-hydroxysalvinolone (**5**) (20 mg), 1-oxosalvibretol (**4**) (15 mg), 1-oxoaethiopinone (8 mg), taxodione (150 mg), ferruginol (15 mg), 7-hydroxytaxodione (**6**) (17 mg), candidissiol (**3**) (20 mg), 11-hydroxy-12-methoxy-8,11,-13-abietatriene (24 mg), 7,7′-bistaxodione (**7**) (12 mg), 11,11′-didehydroxy-7,7′-dihydroxytaxodione (**8**) (18 mg), salvicanaric acid (12 mg), limbinol (8 mg), and salvilimbinol (7 mg).

Salvibretol (1): $[\alpha]^{20}_D$ +7° (*c* 0.1, $CHCl_3$); UV (MeOH) λ max (log ϵ) 335 (3.1), 303 (3.7), 290 (3.8), 240 (4.2) nm; IR ($CHCl_3$) ν max 3450, 3100, 2980, 2920, 2870, 1700, 1620, 1600, 1565, 1500, 1450, 1420, 1370, 1320, 1210, 1170, 1080, 1000, 940 cm^{-1}; ^{1}H- and ^{13}C-NMR data ($CDCl_3$, 300 and 75.4 MHz) see Table 1; HRCIMS *m/z* $[M + 1]^+$ 299.1988 $C_{20}H_{27}O_2$ (calcd 299.2010); EIMS (70 eV) *m/z* $[M]^+$ 298 (65), $[M - 15]^+$ 283 (15), 243 (30), 229 (100), 201 (18), 185 (15), 97 (18), 83 (24), 69 (37).

1-Oxosalvibretol (4): $[\alpha]^{22}_D$ +15.2° (*c* 0.1, $CHCl_3$); UV (MeOH) λ (log ϵ) 336 (3.0), 305 (3.7), 290 (3.7), 245 (4.2) nm; IR ($CHCl_3$) ν max 3450, 3050, 2980, 2860, 1720, 1705, 1610, 1600, 1570, 1510, 1450, 1370, 1210, 1160, 1120, 1090, 1000, 980 cm^{-1}; ^{1}H- and ^{13}C-NMR data ($CDCl_3$, 300 and 75.4 MHz) see Table 1; HREIMS *m/z* $[M]^+$ 312.1744 $C_{20}H_{24}O_3$ (calcd 312.1725); EIMS (70

eV); *m/z* $[M]^+$ 312 (40), $[M - 15]^+$ 297 (10), 243 (100), 224 (25), 152 (10), 128 (18), 108 (13), 69 (5).

6-Hydroxysalvinolone (5): $[\alpha]^{22}_D$ +42° (*c* 0.1, $CHCl_3$); UV (MeOH) λ (log ϵ) 345 (3.0), 287 (3.8), 245 (sh), 210 (4.7) nm; IR ($CHCl_3$) ν max 3400, 3050, 2960, 2920, 2880, 1690, 1660, 1600, 1560, 1460, 1370, 1320, 1210, 1140, 1060, 1000, 750 cm^{-1}; ^1H- and ^{13}C-NMR data ($CDCl_3$, 200 and 50.32 MHz) see Table 1; HRCIMS *m/z* $[M + 1]^+$ 331.1906 $C_{20}H_{27}O_4$ (calcd 331.1909); EIMS (70 eV) *m/z* $[M]^+$ 330 (100), $[M - Me]^+$ 315 (80), 300 (15), 285 (8), 261 (10), 218 (7), 83 (15), 69 (9), 57 (20).

6-Hydroxysalvinolone acetate (5a): IR ($CHCl_3$) ν max 2970, 1725 and 1735, 1680, 1650, 1595, 1560, 1460, 1370, 1310, 1255, 1145, 1060, 995, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.28 and 1.30 (each 3H, d, $J = 7.1$ Hz, H_3-16 and H_3-17), 1.23 and 1.27 (each 3H, s, H_3-18 and H_3-19), 1.65 (3H, s, H_3-20), 2.32 (3H, s, OAc), 2.37 (6H, s, 2 × OAc), 2.98 (1H, dd, $J = 12.6$, 3.0 Hz, H-1β), 8.12 (1H, s, H-14).

7-Hydroxytaxodione (6): $[\alpha]^{22}_D$ +42° (*c* 0.1, $CHCl_3$); UV (MeOH) λ (log ϵ) 460 (sh), 350 (sh), 316 (3.7) nm; IR ($CHCl_3$) ν max 3400 (OH), 3050, 2980, 2820, 1695, 1640, 1630, 1460, 1365, 1300, 1250, 1150, 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) see text; ^{13}C NMR ($CDCl_3$, 50.32 MHz) see Table 2; HREIMS *m/z* $[M]^+$ 330.1822 $C_{20}H_{26}O_4$ (calcd 330.1830); EIMS (70 eV) *m/z* $[M]^+$ 330 (12), $[M - 15]^+$ 315 (10), $[M - 18]^+$ 312 (8), 284 (15), 256 (20), 213 (12), 166 (15), 105 (35), 82 (40), 78 (100).

7,7′-Bistaxodione (7): UV (MeOH) λ (log ϵ) 460 (sh), 360 (sh), 318 (3.8) nm; IR ($CHCl_3$) ν max 3560 (sh), 3430, 2960, 2920, 2880, 1710, 1685, 1610, 1460, 1420, 1370, 1300, 1230, 1050, 980, 900, 810, 760 cm^{-1}; ^1H-NMR ($CDCl_3$, 200 MHz) see text; ^{13}C NMR ($CDCl_3$, 50.32 MHz) see Table 2; HREIMS *m/z* $[M]^+$ $C_{40}H_{50}O_6$ 626.3720 (calcd 626.3727); EIMS (70 eV) *m/z* $[M]^+$ 626 (100), $[M - 15]^+$ 611 (15), $[M - 28]^+$ 598 (20), 583 (15), 555 (10), $[M/2]^+$ 313 (15), 285 (20), 245 (13), 217 (13), 123 (22), 109 (32), 83 (42), 59 (73).

11,11′-Didehydro-7,7′-dihydroxytaxodione (8): UV (MeOH) λ (log ϵ) 460 (sh), 380 (sh), 320 (3.8) nm; IR ($CHCl_3$) ν max 3360, 2960, 2920, 2870, 1715, 1680, 1620, 1460, 1420, 1375, 1300, 1230, 1150, 900, 820, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) see text; ^{13}C NMR ($CDCl_3$, 50.32 MHz) see Table 2; HREIMS *m/z* $[M]^+$ $C_{40}H_{50}O_6$ 626.3722 (calcd 626.3727); EIMS (70 eV) *m/z* $[M]^+$ (100), $[M - 15]^+$ 611 (15), $[M - 28]^+$ 598 (20), 583 (25), 555 (12), $[M/2]^+$ 313 (20), 243 (30), 109 (18), 83 (60), 58 (23).

Acknowledgment. The authors thank Dr. S. W. Pelletier, University of Georgia, Athens, Georgia, for the SINEPT experiments of compounds **1** and **4** and also Dr. Murat Kartal, University of Ankara, for the collection and identification of the plant. One of us (A. U.) thanks the University of Istanbul Research Fund for the partial support of this study (Ö-7).

References and Notes

(1) Ulubelen, A.; Topcu, G. *J. Nat. Prod.* **1992**, *55*, 441−444.
(2) Gill, R. R.; Cordell, G. A.; Topcu, G.; Ulubelen, A. *J. Nat. Prod.* **1994**, *57*, 181−185.
(3) Ulubelen, A.; Topcu, G.; Lotter, H.; Wagner, H.; Eriş, C. *Phytochemistry* **1994**, *36*, 413−415.
(4) Ulubelen, A.; Topcu, G.; Lin, L.; Cordell, G. A. *Phytochemistry* **1992**, *31*, 2419−2421.
(5) Lin, L.-Z.; Blasko, G.; Cordell, G. A. *Phytochemistry* **1989**, *28*, 177−181.
(6) Ulubelen, A.; Topcu, G.; Tan, N. *Tetrahedron Lett.* **1992**, *33*, 7241−7244.
(7) Ulubelen, A.; Topcu, G.; Tan, N. *Phytochemistry* **1992**, *31*, 3637−3638.
(8) Rodriguez, B.; Fernandez-Gadea, F.; Savona, G. *Phytochemistry* **1984**, *23*, 1805−1806.
(9) Gonzales, A. G.; Herrare, J. R.; Luis, J. G.; Ravelo, A. G.; Perales, A. *J. Nat. Prod.* **1987**, *50*, 341−348.
(10) Topcu, G.; Eriş, C.; Ulubelen, A. *Phytochemistry* **1996**, *41*, 1143−1147.
(11) Kupchan, S. M.; Karim, A.; Marcks, C. *J. Am. Chem. Soc.* **1968**, *90*, 5923−5924.
(12) Cambie, R. C.; Madden, R. J.; Parnell, J. C. *Aust. J. Chem.* **1971**, *24*, 217−221.
(13) Burnell, R. H.; Desfossess, S.; Jean, M. *J. Nat. Prod.* **1993**, *56*, 627−628.
(14) Hueso-Rodriguez, J. A.; Rodriguez, J. B.; Savona, G.; Bruno, M. *Phytochemistry* **1983**, *22*, 2005−2008.

NP9602224