Phytochemistry, Vol. 27, No. 6, pp. 1777–1781, 1988.
Printed in Great Britain.

0031-9422/88 $3.00+0.00
Pergamon Press plc.

QUINONE METHIDE DITERPENOIDS FROM THE ROOTS OF *SALVIA TEXANA*

ANTONIO G. GONZÁLEZ, ZAHIRA E. AGUIAR, JAVIER G. LUIS, ANGEL G. RAVELO and XORGE DOMÍNGUEZ*

Centro de Productos Naturales Orgánicos 'Antonio González', Universidad de La Laguna, Tenerife, Canary Islands, Spain, *Instituto Tecnológico y de Estudios Superiores de Monterrey, Monterrey, Mexico

(*Revised received* 19 *October* 1987.)

Key Word Index—*Salvia texana*; Labiatae; quinone methides; diterpenes; 6-deoxo-2α-hydroxytaxodione; 2α-hydroxytaxodione; 2α-hydroxytaxodone; 2α,7-dihydroxytaxodone; salviol.

Abstract—Four new diterpene methylenequinones, 6-deoxo-2α-hydroxytaxodione, 2α-hydroxytaxodione, 2α-hydroxytaxodone and 2α, 7-dihydroxytaxodone, were isolated from the roots of *Salvia texana*. The structure of these natural compounds was established by chemical and spectroscopic means. The known diterpenoid, salviol, was also obtained from the same plant.

INTRODUCTION

As part of a continuing study of the chemical components of the flora used in Latin American popular medicine, *Salvia texana* (Labiatae), collected in Mexico was analysed. The new diterpenic methylenequinones (**1**–**4**) were obtained from the root extract; these compounds are related to taxodione and taxodone isolated [1] from the seeds of *Taxodium distichum* (Taxodiaceae) and which have significant *in vivo* activity against Walker intramuscular carcinosarcoma 256 in rats and *in vitro* activity against cells from human nasopharynx carcinoma (KB) [2].

Although various diterpene *o*-benzoquinones [3–7] and *p*-benzoquinones [8–12] have been isolated from the genus Salvia, methylenequinones are uncommon and the only ones reported recently [13] have been taxodione from *Salvia moorcraftiana* and a phenantrene methylenequinone, fructiculine B [14] from *Salvia fructiculosa*.

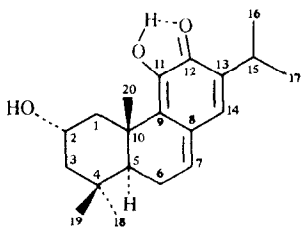
The ^{13}C NMR spectra of these diterpene methylenequinones have not been published previously and so the assignments for **1**, **2** and **4** are listed in Table I.

RESULTS AND DISCUSSION

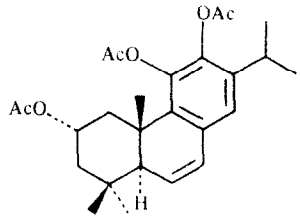
After repeated chromatography of the methanol extract of the roots of *Salvia texana* on Sephadex and silica gel, the following compounds were isolated, in order of ascending polarity. Compound **1** was assigned the molecular formula $C_{20}H_{28}O_3$ and the structure 6-deoxo-2α-hydroxytaxodione on the basis of the following considerations. The IR spectrum showed absorptions for alcohol and phenol groups (3570 and 3305 cm^{-1}) and for a methylenequinone grouping (1597 and 1547 cm^{-1}). The UV spectra showed bands at λ_{max} (EtOH) 315 nm; λ_{max} (EtOH + NaMeO) 315, 290 and 250 nm. In the ^{1}H NMR spectrum, signals for an isopropyl group on an aromatic ring and three angular methyls were observed. The chemical shift of one of the methyls (δ 1.19) was typical of the β-methyl on C-10 in abieta-11,13,18-triene type diterpenes [15–17]. The same spectrum showed two signals of one proton each at δ 1.72 and 7.46, exchangeable with deuterium oxide, assigned to the protons of an alcohol group and a phenol group, respectively. The proton geminal to the alcohol group appeared as a very

Table 1. ^{13}C NMR spectra of compounds **1**, **2** and **4**

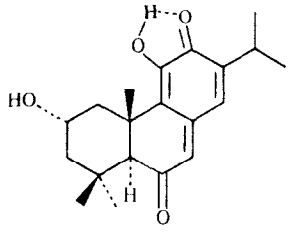
C	1	2	4	C	1	2	4
1	46.2	46.2	45.2	11	143.9	145.2	141.8
2	65.0	64.7	65.2	12	181.5	181.8	199.2
3	50.5	51.5	52.1	13	126.9	124.8	122.3
4	36.6	29.9	35.9	14	136.0	136.0	118.4
5	50.0	62.2	55.6	15	26.7	27.3	27.3
6	25.6	200.3	73.0	16	21.5	23.2	22.4
7	147.9	134.0	147.3	17	21.8	21.8	22.5
8	140.9	130.0	137.3	18	33.4	33.4	36.4
9	131.6	140.0	133.3	19	19.5	21.4	19.7
10	40.1	34.2	42.7	20	23.0	23.2	22.9



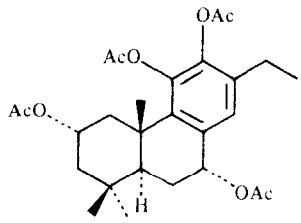
1



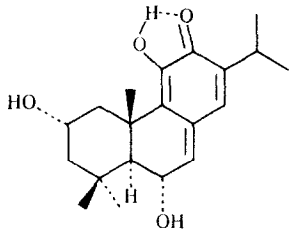
5



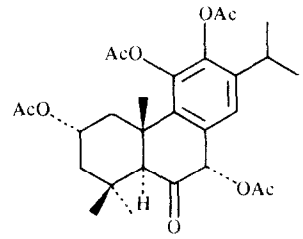
2



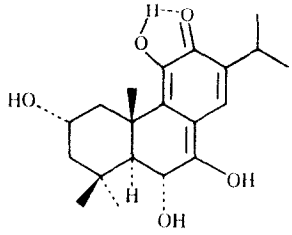
6



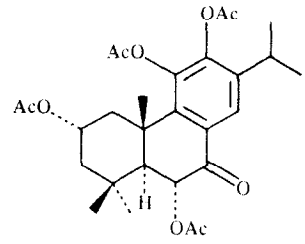
3



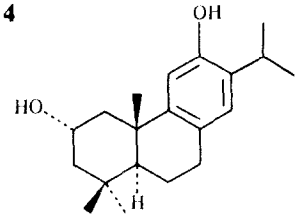
7



4



8



9

broad multiplet centred at δ 4.00; the breadth and multiplicity of this signal were only compatible in this type of diterpene with a 2β-H, the stereochemistry of the alcohol group thus being determined as 2α. Also in the spectrum was a signal for a proton as a singlet at δ 6.80 assignable to the H-14 proton β to the carbonyl. Another proton was observed as a double doublet centred at δ 6.79, (coupling constants, 6.6 and 3.3 Hz),and was attributable to H-7 while a proton appearing as a double doublet centred at δ 1.55, (coupling constants, 11.8 and 3.8 Hz) was due to the H-5. All these data, together with the ^{13}C NMR spectral data (Table 1), are in agreement with the structure and relative stereochemistry given for compound **1**.

Chemical proof of structure **1** for this new compound was forthcoming as treatment of **1** with acetic anhydride in pyridine gave a mixture of two products which were separated by column chromatography on silica gel. The main product **5** upon low resolution mass spectrometry showed the molecular ion $[M]^+$ at m/z 442. In its ^{1}H NMR spectrum it showed signals for one aliphatic and two aromatic acetates, an aromatic proton at δ 6.93 assignable to H-14 and a double bond as an ABX system. The chemical shift of the A and B protons (δ 5.99 and

6.56) indicated a C-6/C-7 double bond allylic to the aromatic ring with the X part of the system assigned to the H-5 proton on the basis of a double resonance experiment. These data are in accordance with structure **5** which derives logically from **1** by the abstraction of a H-6 proton by the base, with consequent tautomerization and acetylation of the phenols.

The minor product, compound **6**, had the molecular ion $[M]^+$ at *m/z* 502. In the ^{1}H NMR spectrum, signals appeared for two aliphatic acetates, two aromatic acetates and a single aromatic proton (δ 7.09). The chemical shift and multiplicity of the proton geminal to one of the aliphatic acetates (δ 5.95, *t*) pointed to it being benzylic on C-7. These data are all in accordance with structure **6**, which is formed from **1** by a Michael-type addition of the anion acetate to the methylenequinone and subsequent acetylation of the phenol groups. The stereochemistry of the acetate group on C-7 is given as α, since the nucleophile attack should take place on the less impeded α-face and because of the chemical shift of the H-14 proton, and it is analogous to that of rosmanol triacetate [18,19], which also possesses a 7α-acetoxy group.

Product **2** had the molecular formula $C_{20}H_{26}O_4$ determined by high resolution mass spectroscopy. The IR spectrum showed bands at 3570 (alcohol OH), 3320 (enol OH), 1660 (quinoid carbonyl) and 1630 and 1610 cm^{-1} (doublet, hydrogen-bonded quinoid carbonyl), which confirmed the presence of a hydroxy-*p*-benzoquin one grouping [20]. However, the UV spectrum (λ_{max} 321, 333 and 400 nm) was more in keeping with a quinone methide functionality [21] and it is virtually superimposable upon that of taxodione [2]. The ^{1}H NMR spectrum showed two secondary methyls as two doublets centred at δ 1.17 and 1.18 ($J = 7$ Hz), which, taken together with a heptet centred at δ 3.07, indicated the presence in the molecule of an isopropyl group on a double bond. This was confirmed by a prominent peak in the mass spectrum *m/z* 269 $[M-18-43]^+$ (due to the loss of H_2O and the isopropyl group). There were also ^{1}H NMR signals for three more angular methyls. A one-proton singlet at δ 2.60 was assigned to the tertiary H-5 proton α to a carbonyl group. The broad multiplet proton centred at δ 3.97 was assignable to the proton geminal to a secondary alcohol group which was established as 2 α or the reasons given for the same phenomenon in compound **1**. In the low-field region, three one-proton singlets appeared. The signal (exchangeable with D_2O) at δ 7.60 was assigned to the enolic hydroxy group. The signals at δ 6.22 and 6.99 were attributed to the protons on the quinone methide system. These data, and the ^{13}C NMR spectrum (Table 1), were completely in agreement with the structure 2α-hydroxytaxodione for compound **2**. When compound **2** was treated with acetic anhydride in pyridine, it gave a pale yellow tri-acetate ketone (**7**), with the molecular ion, $[M]^+$ at *m/z* 516 in the mass spectrum. In the ^{1}H NMR spectrum, two aromatic acetates were observed (δ 2.30 and 2.31), as were two aliphatic acetates (δ 2.05 and 2.25). The geminal proton of one appeared as a singlet at δ 6.32, and this low chemical shift made it benzylic on C-7 and α to the C-6 carbonyl. The presence of the carbonyl was confirmed by the one-proton singlet at δ 2.81 assignable to H-5. The H-14 aromatic proton appeared as a singlet at δ 7.07.

Compound **3**, molecular formula $C_{20}H_{28}O_4$ (high resolution mass spectrometry), had an IR spectrum which, apart from minor differences in the fingerprint area, was superimposable upon that of compound **1**. The UV spectra of both compounds were also superimposable, indicating that the same functional groups and the same chromophore were present in compound **3** as in **1**. The empirical formula, however, showed that **3** had an extra hydroxy group and this was confirmed by the ^{1}H NMR spectrum in which three singlet protons, exchangeable with D_2O, appeared at δ 2.04 (2 × OH) and 7.49 (ArOH). The signal characteristic of the proton geminal to the 2α-hydroxy group was seen at δ 3.96. The position and stereochemistry of the extra hydroxy group were determined as 6α; hence, the H-5 proton appeared as a doublet centred at δ 1.55 ($J = 10.6$ Hz). The H-6 proton, geminal to the alcohol group, appeared as a double doublet centred at δ 4.67 ($J_1 = 10.6$ Hz, $J_2 = 2.6$ Hz) and the H-7 proton was seen as a doublet centred upon δ 6.53 ($J = 2.6$ Hz). Irradiation of H-6 transformed H-5 and H-7 into separate singlets. The coupling constant H-5/H-6 was compatible with H-6 being β-axial and therefore the hydroxy group was α-equatorial. The other H-14 proton of the quinone methide system appeared as a singlet centred on δ 6.82. All these data were in accordance with a 2α-hydroxytaxodone structure for compound **3**.

Product **4**, molecular formula $C_{20}H_{28}O_5$ (high resolution mass spectrometry) possessed one more hydroxy group than **3**. The UV spectrum had absorption maxima which agree with the existence in the molecule of a methylenequinone system [21]. This was borne out by the ^{1}H NMR spectrum where, in addition to the signals for the isopropyl group and angular methyls, there was a signal characteristic of the proton geminal to the 2α-hydroxy group as a broad multiplet centred at δ 4.08 and a doublet proton centred at δ 4.58 ($J = 13$ Hz). These signals, together with a doublet proton centred at δ 1.75 ($J = 13$ Hz), assignable to the tertiary C-5 proton, established that the position and stereochemistry of the other secondary hydroxy group were 6α and that there were no protons on C-7. In the low-field region of the spectrum, only one proton of the quinone methide system was observed and its low chemical shift (to δ 7.58) indicated the presence of a coplanar hydroxy group on C-7. These data and the ^{13}C NMR data (Table 1) were in accordance with the structure 2α,7-dihydroxytaxodone for **4**. This structure was confirmed chemically since treatment of **4** with acetic anhydride in pyridine gave a tetra-acetoxy ketone (**8**) with signals for two aliphatic and two aromatic acetates in the ^{1}H NMR spectrum. The chemical shift of the proton geminal to one of the acetoxy groups, which appeared as a doublet centred at δ 5.81 ($J = 13.4$ Hz), indicated that it was allylic to a carbonyl group. Its coupling with H-5 (double resonance experiments), which appeared as a doublet centred at δ 2.26 ($J = 13.4$ Hz), determined its position on C-6 and the coupling constant revealed its α-equatorial stereochemistry. The chemical shift of the H-14 aromatic proton to δ 8.00 is characteristic of this type of diterpene when there is a carbonyl group on C-7 [22, 23].

Compound **9** proved to be an aromatic diterpene with physical and spectral data completely superimposable upon those reported [24] for salviol and upon those of an authentic sample of salviol [16].

The absolute configurations of compounds **1**–**4** were not determined. However, they are believed to belong to the normal series like salviol (**9**) which co-occur in the same species.

EXPERIMENTAL

^{1}H and ^{13}C NMR: 200 MHz, $CDCl_3$ as solvent and TMS as int. standard. IR:$CHCl_3$. Dry CC was carried out on silica gel, 0.05–0.2 mm. Voucher plant specimens were lodged with the Herbarium of the Department of Botany. Instituto Tecnologicó y de Estudios Superiores de Monterrey, Monterrey, Mexico.

The finely-cut roots of *Salvia texana* (3 kg) were extracted with cold MeOH (5 l) Filtration and evapn of the solvent with a rotavapor *in vacuo* gave a reddish-brown extract (48 g) which was chromatographed on Sephadex using a mixture of *n*-hexane–$CHCl_3$–MeOH (5:5:10) as solvent and 500 ml fractions were collected. Only fractions 40–58 were studied. After repeated chromatography on silica gel using mixtures of *n*-hexane–EtOAc as solvent the following compounds were isolated.

6-Deoxo-2α-hydroxy-taxodione (**1**) Isolated as a brownish-yellow oil (60.5 mg). $[M]^+$ at *m/z* 316.2043 (calcd for $C_{20}H_{28}O_3$, 316.2048); UV λ_{max}^{EtOH} nm: 315, $\lambda_{max}^{EtOH/NaOMe}$ nm: 315, 290, 250, $\lambda_{max}^{EtOH/AlCl_3}$ nm: 280, 228, $\lambda_{max}^{EtOH/AlCl_3/HCl}$ nm: 270, 230; IR ν_{max} cm^{-1} 3570, 3305, 2940, 1597, 1547, 1448, 1430, 1375, 1340, 1290, 1250, 1145, 1025, 973, 950, 925, 910, 895, 835, 800; ^{1}H NMR:δ 0.99, 1.00 (each 3H, *s*, H_3-18, H_3-19), 1.12, 1.13 (each 3H, *d*, J = 7 Hz, H_3-16, H_3-17), 1.19 (3H, *s*, H_3-20), 1.24 (1H, *d*, J = 8 Hz, H-3α), 1.55 (1H, *dd*, J_1 = 11.8 Hz, J_2 = 3.8 Hz, H-5), 1.72 (1H, *br s*,OH) 1.84 (1H, *dq*, H-1α), 2.50 (2H, *m*, 2 × H-6), 3.05 (1H, *hept*, H-15), 3.35 (1H, *dq*, H-1β), 4.00 (1H, *br m*, H-2β), 6.80 (1H, *s*, H-14), 6.79 (1H, *dd*, J_1 = 6.6 Hz, J_2 = 3.3 Hz, H-7), 7.46 (1H, *s*, ArOH). ^{13}C NMR (50 MHz): δ 19.49 (*q*), 21.47 (*q*) (21.77 (*q*), 23.00 (*q*), 25.65 (*t*), 26.73 (*d*), 33.36 (*q*), 34.65 (*s*), 40.10 (*s*), 46.19 (*t*), 50.00 (*d*), 50.50 (*t*), 64.98 (*d*), 126.29 (*s*), 131.56 (*s*), 136.00 (*d*), 140.88 (*s*), 143.90 (*s*), 147.94 (*d*), 181.50 (*s*), EIMS *m/z* (rel. int.): 316 $[M]^+$ (9), 298 (23), 283 (13), 273 (3), 265 (2), 260 (7), 255 (7), 229 (18), 204 (18), 157 (15), 115 (25), 91 (25), 57 (53), 55 (54), 43 (100).

Acetylation of 6-deoxo-2α-hydroxytaxodione (**1**). Compound **1** (27.8 mg) was treated with Ac_2O (1 ml) in pyridine (2 ml) overnight at room temp and after work-up and silica gel CC separation, using *n*-hexane–EtOAc (7:3) gave 2α,11,12-triacetoxy-abieta-6,8,11,13-tetraene (**5**) as a pale yellow oil (18 mg): ^{1}H NMR:δ 1.05, 1.13 (each 3H, *s*, H_3-18, H_3-19), 1.18, 1.23 (each 1H, *d*, J = 7 Hz, H_3-16, H_3-17), 1.21 (3H, *s*, H_3-20), 2.07 (3H, *s*, OAc), 2.27, 2.30 (each 3H, *s*, 2 × ArOAc), 2.29 (1H, *t*, J = 3 Hz, H-5), 2.91 (2H, *m*, H-15 and H-1β), 5.11 (1H, *br m*, H-2β), 5.99 (1H, *dd*, J_1 = 10 Hz, J_2 = 3 Hz, H-6), 6.56 (1H, *dd*, J_1 = 10 Hz, J_2 = 3 Hz, H-7), 6.93 (1H, *s*, H-14); EIMS *m/z* (rel. int.): 442 $[M]^+$ (90), 414 (28), 400 (46), 397 (17), 382 (25), 367 (14), 341 (50), 340 (42), 299 (13), 257 (12); and 2α,7α,11, 12-tetracetoxy-abieta-8,11,13-triene (**6**) as a colourless oil (6 mg): ^{1}H NMR:δ 0.98 (6H, *s*, H_3-18, H_3-19), 1.15, 1.19 (each 1H, *d*, J = 7 Hz, H_3-16, H_3-17), 1.25 (3H, *s*, H_3-20), 2.04, 2.08 (each 3H, *s*, 2 × OAc), 2.29, 2.30 (each 3H, *s*, 2 × ArOAc), 2.89 (1H, *m*, H-15), 5.00 (1H, *br m*, H-2β), 5.95 (1H, *t*, H-7), 7.09 (1H, *s*, H-14); EIMS *m/z* (rel. int.): 502 $[M]^+$ (12), 440 (6), 400 (6), 398 (5), 358 (64), 345 (6), 341 (17), 328 (16), 325 (10), 314 (23), 299 (47), 288 (97), 242 (54), 167 (24).

2α-Hydroxytaxodione (**2**). Isolated as a reddish-brown oil (40 mg); $[M]^+$ at *m/z* 330.1837. (Calcd for $C_{20}H_{26}O_4$, 330.1843); UV λ_{max}^{EtOH} nm 400, 333, 321, $\lambda_{max}^{EtOH+NaMeO}$ nm; 355, 313, 248 $\lambda_{max}^{EtOH+AlCl_3}$ nm: 330, 316, 222, $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm: 335, 226; IR ν_{max} cm^{-1}; 3570, 3320, 2980, 2940, 2900, 2850, 1660, 1630, 1610, 1600, 1585, 1500, 1450, 1410, 1375, 1340, 1290, 1275, 1255, 1230, 1140, 1095, 1075, 1025, 1010, 985, 975, 895, 835, 800; ^{1}H NMR:δ 1.17, 1.18 (each 3H, *d*, J = 7 Hz, H_3-16, H_3-17), 1.19 (3H, *s*, H_3-18), 1.31, 1.32, (each 3H, H_3-19, H_3-20), 2.60 (1H, *s*, H-5), 3.07 (1H, *hept*, H-15), 3.25 (1H, *br d*, H-1β), 3.97 (1H, *br m*, H-2β), 6.22 (1H, *s*, H-14), 6.99 (1H, *s*, H-7), 7.60 (1H, *s*, OH); ^{13}C NMR (50 MHz): δ 21.4 (*q*), 21.8 (*q*), 23.0 (*q*), 23.2 (*q*), 27.3 (*d*), 29.9 (*s*), 33.4 (*q*), 34.2 (*s*), 46.2 (*t*), 51.5 (*t*), 62.2 (*d*), 64.7 (*d*), 124.8 (*s*), 130.0 (*s*), 134.0 (*d*), 136.0 (*d*), 140.0 (*s*), 145.2 (*s*), 181.8 (*s*), 200.3 (*s*), EIMS *m/z* (rel. int.): 330 $[M]^+$ (15), 312 (17), 297 (16), 284 (5), 279 (5), 269 (25), 258 (45), 243 (16), 227 (55), 215 (15), 213 (14), 206 (27), 115 (30), 43 (100).

Acetylation of 2α-hydroxytaxodione (**2**) Compound **2** (31.8 mg) was treated with Ac_2O (1 ml) in pyridine (2 ml) overnight at room temp. After work-up, 7-oxo-2α,7α, 11, 12-tetracetoxy-abieta-8,11,13-triene (**7**) was obtained as a pale yellow oil (30 mg): ^{1}H NMR:δ 1.06, 1.21 (each 3H, *s*, H_3-18, H_3-19), 1.17, 1.19 (each 3H, *d*, J = 7 Hz, H_3-16, H_3-17), 1.31 (3H, *s*, H_3-20), 2.05, 2.25 (each 3H, *s*, 2 × OAc), 2.30, 2.31 (each 3H, *s*, 2 × ArOAc), 2.81 (1H, *s*, H-5), 2.91 (1H, *hept*, H-15), 3.13 (1H, *dq*, H-1β), 5.02 (1H,*br m*, H-2), 6.32 (1H, *s*, H-7), 7.07 (1H, *s*, H-14): EIMS *m/z* (rel. int.): 516 $[M]^+$ (20), 475 (12), 474 (43), 446 (2), 432 (38), 414 (13), 404 (6), 390 (7), 372 (33), 370 (25), 344 (10), 330 (38), 315 (10), 297 (24), 230 (29), 219 (17), 141 (10), 129 (16), 55 (100).

2α-Hydroxytaxodone (**3**). Isolated as a yellow oil (16.5 mg). $[M]^+$ at *m/z* 332.1989 (calcd for $C_{20}H_{28}O_4$, 332.1994); ^{1}H NMR:δ 1.13, 1.15 (each 1H, *d*, J = 7 Hz, H_3-16, H_3-17) 1.20, 1.24, 1.27 (each 3H, *s*, 3 × Me), 1.55 (1H, *d*, J = 10.6 Hz, H-5), 2.04 (2H, *br m*, 2 × OH), 3.05 (1H, *hept*, H-15), 3.28 (1H, *dq*, H-1β), 3.96 (1H, *br m*, H-2β), 4.67 (1H, *dd*, J_1 = 10.6 Hz, J_2 = 2.6 Hz, H-6), 6.53 (1H, *d*, J = 2.6 Hz, H-7), 6.82 (1H, *s*, H-14), 7.49 (1H, *s*, ArOH); EIMS *m/z* (rel. int.): 332 $[M]^+$ (1), 317 (45), 314 (6), 300 (8), 299 (34), 285 (5), 281 (2), 271 (8), 258 (9), 255 (7), 243 (20), 239 (12), 229 (13), 217 (10), 115 (38), 107 (13), 91 (44), 55 (100).

2α,7-Dihydroxytaxodone (**4**). Isolated as a yellow oil (80.5 mg); $[M]^+$ at *m/z* 348.1940 (calcd for $C_{20}H_{28}O_5$, 348.1943); UV λ_{max}^{EtOH} nm 378, 360, 315, 285, 260, $\lambda_{max}^{EtOH+NaMeO}$ nm:365, 315, 257, $\lambda_{max}^{EtOH+AlCl_3}$ nm:380, 325, 270, $\lambda_{max}^{EtOH+AlCl_3+HCl}$ nm:320, 270, 240; ^{1}H NMR:δ 1.21, 1.23 (each 1H, *d*, J = 7Hz, H_3-16, H_3-17), 1.24 (6H, *s*, H_3-18, H_3-19), 1.52 (3H, *s*, H_3-20), 1.75 (1H, *d*, J = 13 Hz, H-5), 1.83 (1H, *br s*, -OH), 3.06 (1H, *hept*, -H-15), 3.70 (1H, *br s*, -OH), 3.72 (1H, *m*, H-1β), 3.85 (1H, *br s*, -OH), 4.08 (1H,*br m*, H-2β), 4.58 (1H, *d*, J = 13 Hz, H-6), 7.58 (1H, *s*, H-14); ^{13}C NMR (50 MHz):δ 19.69 (*q*), 22.36 (*q*), 22.49 (*q*), 22.88 (*q*), 27.25 (*d*), 35.90 (*s*), 36.45 (*q*), 42.72 (*s*), 45.23 (*t*), 52.12 (*t*), 55.56 (*d*), 65.21 (*d*), 73.05 (*d*), 118.42 (*d*), 122.28 (*s*), 133.27 (*s*), 137.32 (*s*), 141.81 (*s*), 147.26 (*s*), 199.21 (*s*); EIMS *m/z* (rel. int.): 348 $[M]^+$ (3), 330 (20), 315 (53), 312 (10), 303 (7), 301 (100), 297 (14), 287 (6), 269 (4), 247 (9), 231 (8), 219 (19), 189 (10), 187 (5), 177 (8), 157 (5), 141 (5), 115 (12), 91 (13), 83 (50).

Acetylation of 2α, 7-dihidroxytaxodone (**4**). Compound **4** (14 mg) dissolved in pyridine (2 ml) was treated with Ac_2O (1 ml) and left to stand overnight at room temp. After work-up, 7-oxo-2α,6α,11,12-tetracetoxy-abieta-8,11,13-triene (**8**) was obtained as a pale yellow oil (10 mg): ^{1}H NMR:δ1.13 (3H, *s*, H_3-18), 1.17, 1.19 (each 3H, *d*, J = 7 Hz, H_3-16, H_3-17), 1.21 (3H, *s*, H_3-19), 1.56 (3H, *s*, H_3-20), 1.78 (1H, *dq*, H-1α), 2.05, 2.25 (each 3H, *s*, 2 × OAc), 2.26 (1H, *d*, J = 13.4 Hz, H-5), 2.31 (6H, *s*, 2 × ArOAc), 2.90 (1H,*br m*, H-15), 3.13 (1H, *br dd*, H-1β), 5.02 (1H, *br m*, H-2β), 5.81 (1H, *d*, J = 13.4 Hz, H-6), 8.00 (1H, *s*, H-14); EIMS *m/z* (rel. int.): 516 $[M]^+$ (4), 474 (1), 458 (1), 432 (2), 414 (2), 372 (16), 354 (2), 330 (8), 312 (27), 297 (21), 283 (8), 232 (4), 219 (6), 205 (12), 149 (11), 128 (5), 85 (64), 83 (100).

Acknowledgements–We thank the CAICYT for Grants Nos 069–84 and PB85–0171 and the AIETI Foundation (Madrid) for financial support. Z.E.A. is indebted to the AIETI Foundation for a Fellowship.

REFERENCES

1. Kupchan, S. M., Karim, A. and Marcks, C. (1968) *J. Am. Chem. Soc.* **90**, 5923.

2. Kupchan, S. M., Karim, A. and Marcks, C. (1969) *J. Org. Chem.* **34**, 3912.
3. Romanova, A. S., Patudin, A. V. and Bankovskii, A. J. (1977) *Khim. Prir. Soedin* **13**, 414.
4. Fang, C. N., Chang, P. L. and Hsu, T. P. (1876) *Yao Hsueh Hsueh Pao* **34**, 197.
5. Xu, X. M. and Xiao, Z. Y. (1984) *Chung Ts'ao Yao* **15**, 1.
6. Chien, M. K., Yang, P. C. and Chin, K. O. (1980) *Yao Hsueh T'ung Pao* **15**, 1
7. Romanova, A. S., Patudin, A. V., Pervykh, L. N. and Zobenko, L. P. (1978) *Khim. Prir. Soedin* **14**, 515.
8. Patudin, A. V. and Romanova, A. S. (1976) *Khim. Farm. Zh.* **11**, 90.
9. Mukherjee, K. S., Ghosh, P. K. and Badruddoza, S. (1981) *Phytochemistry* **20**, 1441.
10. Mukherjee, K. S., Ghosh, P. K. and Mukherjee, R. K. (1983) *Phytochemistry* **22**, 1296.
11. Bakshi, B., Hassarajani, S. A., Mulchandani, N. B. and Shankar, J. (1984) *Planta Med.* 355.
12. Romanova, A. S., Pribylova, G. F., Patudin, A. V., Leskova, E. S., Pakalu, D. A. and Bankovskii, A. J. (1972) *Khim. Prir. Soedin* **2**, 237.
13. Simões, F., Michavila, A., Rodriguez, B., Garcia-Alvarez, M. C. and Mashooda, H. (1986) *Phytochemistry* **25**, 755.
14. Rodriquez-Hahn, L., Esquivel, B., Sanchez, C., Cardenas, J., Estebanes, L., Soriano-Garcia, M., Toscano, R. and Ramamoorthy, T. P. (1986) *Tetrahedron Letters* **27**, 5459.
15. González, A. G., Rodriguez, C. M. and Luis, J. G. (1987) *Phytochemistry* **26**, 1471.
16. González, A. G., Fraga, B. M., Luis, J. G. and Ravelo, A. G. (1975) *An. Quim.* **71**, 701.
17. Escudero, J., Pérez, L., Rabanal, R. M. and Valverde, S. (1983) *Phytochemistry* **22**, 585.
18. Inatani, R., Nakatani, N., Fuwa, H. and Seto, H. (1982) *Agric. Biol. Chem.* **46**, 1661.
19. Fraga, B. M., González, A. G., Herrera, J. R., Luis, J. G., Perales, A. and Ravelo, A. G. (1985) *Phytochemistry* **24**, 1853.
20. Bycroft, B. W. and Roberts, J. C. (1963) *J. Org. Chem.* **28**, 1429.
21. Turner, A. B. (1966) *Prog. Chem. Org. Nat. Prod.* **24**, 288.
22. González, A. G., Fraga, B. M., Luis, J. G. and Ravelo, A. G. (1973) *Experientia* **29**, 1471.
23. Lickei, A. E., Rieke, A. C. and Wheeler, D.M.S. (1967) *J. Org. Chem.* **32**, 1647.
24. Hayashi, T., Handa, T., Ohashi, M. and Makisawa, H. (1971) *Chem. Comm.* 541.