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DITERPENOID TOTAL SYNTHESIS—XIII*

TAXODIONE, A QUINONE METHIDE TUMOR INHIBITOR

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Abstract—Podocarpic acid was converted to taxodione. Since the total synthesis of the former is recorded, this conversion implies a total synthesis of the latter.

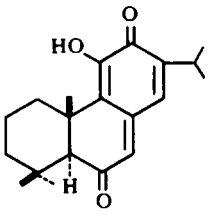
TAXODIONE (I) is a diterpene with abietane skeleton recently isolated from *Taxodium distichum* Rich (Taxodiaceae).[1,2] Its synthesis attracted our attention mainly because of its unique structure (I) as a quinone methide and partly because of its significant tumor-inhibitory activity against the Walker carcinosarcoma in rats. The present paper is concerned with the successful synthesis of this novel natural product.

During the course of their structure elucidation, Kupchan *et al.* converted taxodione (I) into 11,12-dimethoxyabieta-8,11,13-triene (XVII) which confirmed the carbon skeleton of I.[1,2] Reversal of this transformation is obviously the simplest solution of the synthetic problem. Functionalization at C-6 of diterpenes related to podocarpic acid has been reported in a previous part of this series.[3] A considerable amount of work was necessary, however, to prepare the key-intermediate (XVII) in quantity.

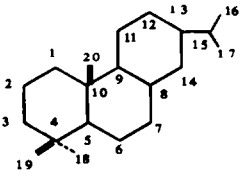
Commercially available podocarpic acid (II) was chosen as our starting material. Since its total synthesis has been achieved,[4,5] any synthesis starting from this acid can be regarded as a formal total synthesis. Conversion of methyl O-methylpodocarpate (III)[6] into methyl 12-methoxyabieta-8,11,13-trien-19-oate (VII) via IV, V and VI was carried out as described by Campbell and Todd.[7,8] They also reported its transformation to 12-methoxyabieta-8,11,13-trien-19-al (IX) by the Rosenmund reduction of an acyl chloride derived from X.[9] An alternative route was chosen in the present work. The ester (VII) was reduced to the known alcohol (VIII)[10] which was oxidized with the Sarett chromic anhydride-pyridine reagent[11] to give the aldehyde (IX) in an excellent yield together with a small amount of the acid (X). The aldehyde (IX) was reduced by the Wolff-Kishner method to give a mixture of ferruginol methyl ether (XI) and ferruginol (XII).[9,12] The mixture was boiled with hydrobromic-hydriodic acids and the product was benzoylated to give crystalline ferruginol benzoate (XIII).[9,12] Since the original work[7,9] was carried out at the time when neither IR nor NMR spectroscopic methods were available, the spectral data of the intermediates are recorded in the Experimental.

The conversion of ferruginol benzoate (XIII) into the key intermediate (XVII) via XIV, XV and XVI was carried out as described.[13] Acetoxylation at C-7 of XVII with lead tetraacetate gave a crystalline acetate (XVIII). This was dissolved in acetic acid and the solution was heated under reflux to afford an oily olefin (XIX). *m*-Chloro-

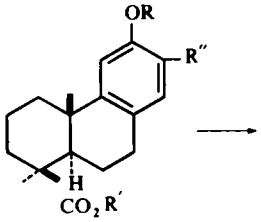
* Part XII, K. Mori and M. Matsui, *Agr. Biol. Chem.* (Japan) **34**, (1970)



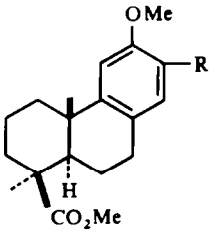
I



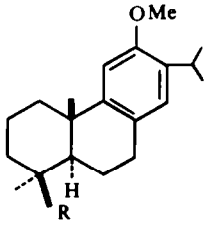
abietane



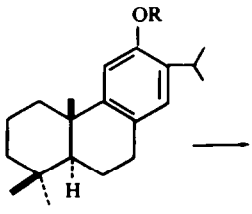
	R	R′	R″
II	H	H	H
III	Me	Me	H
IV	Me	Me	COMe



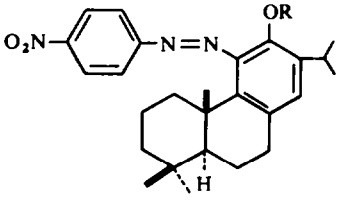
V: R = $C(OH)Me_2$
VI: R = $C(=CH_2)Me$
VII: R = $CHMe_2$



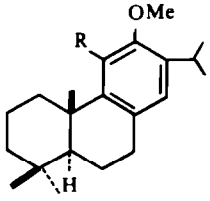
VIII: R = CH_2OH
IX: R = CHO
X: R = CO_2H



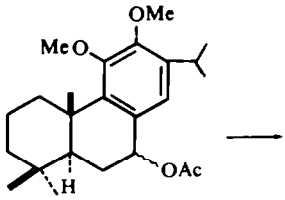
XI: R = Me
XII: R = OH
XIII: R = $OCOC_6H_5$



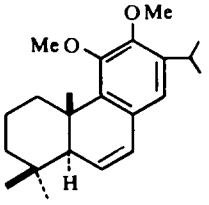
XIV: R = H
XV: R = Me



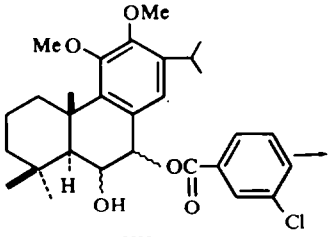
XVI: R = NH_2
XVII: R = OMe



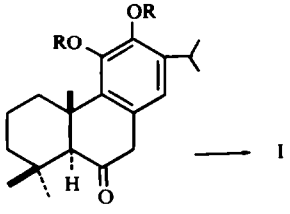
XVIII



XIX



XX



XXI: R = Me
XXII: R = H

perbenzoic acid smoothly oxidized the olefin (XIX) with subsequent cleavage of the initially formed epoxide ring to give a stereoisomeric mixture of diol mono-*m*-chlorobenzoates (XX). This was pyrolyzed at 230–245° to afford pure crystalline 11,12-dimethoxyabieta-8,11,13-trien-6-one (XXI) after chromatographic purification.

Its demethylation was successfully carried out with boron tribromide in dichloromethane[14] to give a diol (XXII). The diol (XXII) dissolved in chloroform was oxidized with silver oxide[15] to afford the final product, taxodione (I), as golden crystals. The synthetic product was identical in every respect (m.m.p., IR, NMR, MS and TLC) with the natural product.* Especially its characteristic NMR spectrum measured as a benzene-d_6 solution was superimposable on that of the authentic taxodione.

The NMR spectral data of the synthetic compounds are listed in Tables 1 and 2. Assignment of the C-20 protons in podocarpic acid derivative is based on the work of Spencer *et al.* who report the shielding effect of the ester carbonyl group on the C-20 protons.[16] In 12-methoxyabieta-8,11,13-trien-19-ol (VIII), however, the C-20 protons are expected to absorb at a lower field than those at C-18, for the hydroxyl O atom deshields the C-18 protons as reported by Wenkert *et al.*[17] Assignment of the C-20 protons in abieta-8,11,13-trienes with two Me groups at C-4 is based on the work of Wenkert, *et al.* who have shown that the C-20 protons absorb at ca. 0·3 ppm down field than those of other Me groups at C-4.[13]

TABLE 1. NMR DATA FOR SYNTHETIC INTERMEDIATES OF PODOCARPIC ACID-TYPE*

Compd	C-CH_3 C-16 and 17		C-18	C-20	CH_2 C-7	CH C-15	O-CH_3 at C-12 or C-19		Aromatic H		Other H
III			1·25	1·02	2·75		3·58	3·68	6·50–	6·92	
			3H, s	3H, s	2H, m		3H, s	3H, s	3H,	ABC	
IV	2·55		1·28	1·06	2·80		3·61	3·80	6·76	7·36	
	3H, s		3H, s	3H, s	2H, m		3H, s	3H, s	1H, s	1H, s	
V	1·60		1·29	1·05	2·80		3·68	3·88	6·85	7·01	
	6H, s		3H, s	3H, s	2H, m		3H, s	3H, s	1H, s	1H, s	
VI	2·08		1·28	1·06	2·75		3·60	3·68	6·68	6·80	$=CH_2$ at C-17
	3H, s		3H, s	3H, s	2H, m		3H, s	3H, s	1H, s	1H, s	5·01, 2H, br.s
VII	1·18	1·19	1·28	1·06	2·75	3·20	3·60	3·72	6·65	6·78	
	3H, d[b]	3H, d[b]	3H, s	3H, s	2H, m	1H, sept[b]	3H, s	3H, s	1H, s	1H, s	
VIII	1·18	1·19	1·05	1·20	2·77	3·18	3·71		6·64	6·75	CH_2OH, 2H ABq
	3H, d[b]	3H, d[b]	3H, s	3H, s	2H, m	1H, sept[b]	3H, s		1H, s	1H, s	centered at 3·65[c]
IX	1·12	1·13	1·21	1·07	2·80	3·17	3·71		6·63	6·77	CHO
	3H, d[b]	3H, d[b]	3H, s	3H, s	2H, m	1H, sept[b]	3H, s		1H, s	1H, s	9·80, 1H, s
X	1·18	1·19	1·34	1·15			3·76		6·66	6·80	
	3H, d[b]	3H, d[b]	3H, s	3H, s			3H, s		1H, s	1H, s	

[a] Values are given in δ units with TMS as an internal standard at 100 MHz. The solvent was $CDCl_3$

[b] $J \simeq 7$ Hz

[c] δH_A 3·45, δH_B 3·78, $J_{AB} = 10$ Hz

* Kindly sent to us by Professor S. M. Kupchan.

TABLE 2. NMR DATA FOR SYNTHETIC TAXODIONE AND INTERMEDIATES OF FERRUGINOL-TYPE[a]

Compd (Solvent)	CH C-5	CH C-6	CH C-7	C-11, C-12 Substituents	CH C-14	CH C-15	C-CH$_3$ C-16,	C-17	C-18,	C-19	C-20	
I	2·29	—	5·29	7·59, 1H, s	6·33	2·95	0·97	1·02	1·17,	1·24,	1·36	
(C_6D_6)	1H, s		1H, s	C-11 OH[b]	1H, s	1H, sept[c]	3H, d[c]	3H, d[c]	3H, s	3H, s	3H, s	
I	2·58	—	6·16	7·51, 1H, s	6·83	2·98	1·16	1·18		1·11	1·26	
($CDCl_3$)	1H, s		1H, s	C-11 OH[b]	1H, s	1H, sept[c]	3H, d[c]	3H, d[c]		3H, s	6H, s	
XII			2·70		6·60	3·08	1·18	1·19	0·92	0·94	1·13	6·35, 1H, s
(CCl_4)			2H, m		1H, s	1H, sept[c]	3H, d[c]	3H, d[c]	3H, s	3H, s	3H, s	C-11
XIII			2·92	7·40–8·25, 5H	6·97	2·92	1·23	1·24	0·98	1·00	1·25	6·97, 1H, s
($CDCl_3$)			2H, m	$OCOC_6H_5$	1H, s	1H	3H, d[c]	3H, d[c]	3H, s	3H, s	3H, s	C-11
XIV			2·73	7·68–8·33, 4H	6·92	3·25	1·23		1·00	1·62		
($CDCl_3$)			2H, m	$=N-C_6H_4NO_2$	1H, s	1H, sept[c]	6H, d[c]		6H, s	3H, s		
XV			2·80	7·91–8·40, 4H $=N-C_6H_4NO_2$	6·91	3·28	0·94,	0·99	1·21	1·28	1·35	
($CDCl_3$)			2H, m	3·44, 3H, s C-12 OCH_3	1H, s	1H, sept[c]	3H, s	3H, s	3H. s	3H, s	3H, s	
XVI			2·75	3·66, 3H, s,	6·28	3·16	1·18		0·92	0·94	1·31	~3·65, 2H, m
($CDCl_3$)			2H, m	C-12 OCH_3	1H, s	1H, sept[c]	6H, d[c]		3H, s	3H, s	3H, s	$-NH_2$
XVII			2·75	3·69 3·78	6·54	3·16	1·13	1·18	0·90	0·92	1·26	
($CDCl_3$)			2H, m	3H, s 3H, s	1H, s	1H, sept[c]	3H, d[c]	3H, d[c]	3H, s	3H, s	3H, s	
XVIII			5·83	3·74 3·82	6·74	3·20	1·17	1·20	0·96	1·25		2·06, 3H, s
($CDCl_3$)			1H, br	3H, s 3H, s	1H, s	1H, sept[c]	3H, d[c]	3H, d[c]	6H, s	3H. s		$OCOCH_3$
XIX	2·16	5·85	6·40	3·80	6·62	3·25	1·17	1·19	0·98	1·05	1·26	
($CDCl_3$)	1H, br	1H, q	1H, q	6H, s	1H, s	1H, sept[c]	3H, d[c]	3H, d[c]	3H, s	3H, s	3H, s	
XXI	2·61	—	3·50	3·76 3·85	6·56	3·15	1·23	1·25	1·08	1·30	1·40	
($CDCl_3$)	1H, s		2H, q[d]	3H, s 3H, s	1H, s	1H, sept[c]	3H, d[c]	3H, d[c]	3H, s	3H, s	3H, s	
XXII	2·64	—	3·51	5·89[b] 5·10[b]	6·35	3·15	1·22	1·23	1·01	1·27	1·35	
($CDCl_3$)	1H, s		2H, q[e]	1H, s 1H, br	1H, s	1H, sept[c]	3H, d[c]	3H, d[c]	3H, s	3H, s	3H, s	

[a] Values are given in δ units with TMS as an internal standard at 100 MHz

[b] Signals disappeared upon D_2O addition

[c] $J = 7$ Hz

[d] AB_q, δ_{H_A} 3·32, δ_{H_B} 3·67, $J_{AB} = 20$ Hz

[e] AB_q, δ_{H_A} 3·32, δ_{H_B} 3·70, $J_{AB} = 20$ Hz

EXPERIMENTAL

All m.ps were uncorrected. IR spectra refer to Nujol mulls for crystalline samples and films for gums unless otherwise stated and were measured with a JASCO IR-E spectrometer. NMR spectra were measured with a JEOL NM-4H 100 spectrometer at 100 MHz in $CDCl_3$ with TMS as an internal standard.

Methyl 0-methylpodocarpate (III). This was prepared from podocarpic acid (Aldrich Chemical Co., Inc., No. 11, 979–2). ν_{max} 1715 (vs), 1605 (s), 1590 (w), 1515 (s), 1260 (s), 1220 (s), 1200 (s), 1155 (s), 1050 (s), 820 (s) cm^{-1}.

Methyl-0-methyl-13-acetylpodocarpate (IV). ν_{max} 1710 (vs), 1660 (vs), 1600 (s), 1560 (w) cm^{-1}.

Methyl 12-methoxy-15-hydroxyabieta-8,11,13-trien-19-oate (V). ν_{max} ~3700 (s), 1705 (vs), 1610 (m), 1570 (w) cm^{-1}.

Methyl 12-methoxyabieta-8,11,13,15-tetraen-19-oate (VI). ν_{max} 1715 (vs), 1640 (m), 1610 (m), 1570 (w), 890 (s) cm^{-1}.

Methyl 12-methoxyabieta-8,11,13-trien-19-oate (VII). ν_{max} 1715 (vs), 1610 (m), 1570 (w) cm^{-1}.

12-Methoxyabieta-8,11,13-trien-19-ol (VIII). ν_{max} ~3400 (s), 1610 (m), 1570 (w), 1245 (vs), 1060 (s), 900 (s), 865 (s) cm^{-1}.

12-Methoxyabieta-8,11,13-trien-19-al (IX) *and 12-methoxyabieta-8,11,13-trien-19-oic acid* (X). A soln of VIII (16·0 g) in dry pyridine (80 ml) was added to an ice-cooled suspension of CrO_3-C_5H_5N complex (prepared from 22·0 g of CrO_3 and 240 ml C_5H_5N) with shaking. The mixture was left at room temp for 1 hr, poured into ice-water, diluted with ether-benzene and filtered through Celite. The organic layer was separated and the aqueous layer was extracted with ether-benzene. The combined organic soln was washed with water, 5% HCl aq, 2N NaOH and sat NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 15·1 g (94%) of crystalline IX. Recrystallization from EtOH gave prisms, m.p. 134–135°; ν_{max} 2750 (m), 1710 (s), 1610 (m), 1570 (w), 1245 (vs), 1060 (s), 900 (s), 865 (s) cm^{-1}. (Found: C, 80·36; H, 9·63. Calc. for $C_{21}H_{30}O_2$: C, 80·21; H, 9·62%). The acid X (0·2 g) was obtained from the NaOH soluble part after conventional work-up. Recrystallization from EtOH gave prisms, m.p. 182–183°; ν_{max} ~3400–~2600 (m), 1690 (vs), 1610 (m), 1575 (w) cm^{-1}. (Found: C, 76·54; H, 9·15. Calc. for $C_{21}H_{30}O_3$: C, 76·32; H, 9·15%).

12-Hydroxyabieta-8,11,13-triene (*ferruginol*, XII). ν_{max} ~3400 (s), 1610 (m), 1570 (w) cm^{-1}.

12-Benzoyloxyabieta-8,11,13-triene (*ferruginol benzoate*, XIII). 1730 (vs), 1600 (m), 1580 (w), 1265 (vs), 1240 (vs), 1160 (s), 1080 (s), 1055 (s), 1020 (s), 890 (m), 700 (vs) cm^{-1}.

11-(p-Nitrophenylazo)-12-hydroxyabieta-8,11,13-triene (XIV). 1610 (w), 1590 (w), 1560 (w), 1520 (s), 1345 (vs), 1155 (m), 1110 (m), 860 (s) cm^{-1}.

11-(p-Nitrophenylazo)-12-methoxyabieta-8,11,13-triene (XV). 1610 (w), 1590 (w), 1525 (s), 1350 (vs), 1030 (s), 880 (m), 860 (m), 850 (m) cm^{-1}.

11-Amino-12-methoxyabieta-8,11,13-triene (XVI). This compound, previously described as an oil,[13] was obtained in two crystalline forms. The azo dye (XV, 5·8 g) was reduced as reported by Brieskorn *et al.*[13] to give an oil which was chromatographed on alumina (Merck, Activity Grade I, neutral, 100 g) in n-hexane. Elution with benzene–n-hexane (1 :1, 1 liter) gave 2·7 g (66%) of XVI as crystals. Recrystallization from MeOH yielded fine prisms, m.p. 142–143°; ν_{max} 3550 (w), 3450 (w), 1605 (s), 1410 (s), 1320 (m), 1210 (m), 1150 (m), 1010 (s), 840 (m) cm^{-1}. (Found: C, 80·44; H, 10·53; N, 4·14. $C_{21}H_{33}ON$ requires: C, 79·94; H, 10·54; N, 4·44%). Another crystalline form, needles from MeOH, m.p. 101–102°, was also obtained. (Found: C, 80·50; H, 10·50; N, 4·21. $C_{21}H_{33}ON$ requires: C, 79·94; H, 10·54; N, 4·44%).

11,12-Dimethoxyabieta-8,11,13-triene (XVII). The yield of this compound was considerably improved by employing the pure crystalline XVI as starting material. The amine (XVI, 2·4 g) was diazotized and solvolyzed in MeOH to give an oil which was chromatographed on alumina (Merck, Activity Grade I, neutral, 100 g) in n-hexane. Elution with ether–n-hexane (1 :4, 300 ml) gave 1·8 g (72%) of crystalline XVII. Recrystallization from MeOH gave needles, m.p. 86–87°; ν_{max} 1600 (w), 1560 (w), 1400 (s), 1325 (s), 1300 (s), 1060 (s), 1020 (vs), 1010 (s) cm^{-1}. (Found: C, 80·34; H, 10·37. Calc. for $C_{22}H_{34}O_2$: C, 79·95; H, 10·37%).

7-Acetoxy-11,12-dimethoxyabieta-8,11,13-triene (XVIII). Lead tetracetate (2·0 g) was added to a soln of XVII (1·471 g) in AcOH (12 ml). The mixture was stirred and heated on a boiling water bath for 30 min under N_2. After cooling, a few drops of ethylene glycol was added to the mixture to destroy excess of $Pb(OAc)_4$. The mixture was diluted with water and extracted with ether. The extract was washed with water, $NaHCO_3$ aq and sat NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was triturated with light petroleum to give 448 mg (27%) of crystalline XVIII. The mother liquor, exhibiting a C=O absorption in its IR spectrum, weighed 1·061 g and was assumed to be a mixture of XVII and XVIII. Recrystallization of the crude crystals from EtOAc-light petroleum gave rhombs, m.p. 146–148°; ν_{max} 1720 (vs), 1600 (w),

1560 (w), 1240 (vs), 1020 (vs), 1005 (vs) cm^{-1}. (Found: C, 74·31; H, 9·47. $C_{24}H_{36}O_6$ requires: C, 74·19; H, 9·34%).

11,12-*Dimethoxyabieta*-6,8,11,13-*tetraene* (XIX). A soln of XVIII (440 mg) in AcOH (10 ml) was heated under reflux for 17 hr under N_2. The solvent was removed *in vacuo* and the residue was dissolved in ether. The ethereal soln was washed with $NaHCO_3$ aq and sat NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 337 mg (84%) of oily XIX, ν_{max} 1600 (w), 1550 (w), 1300 (vs), 1220 (m), 1060 (s), 1020 (vs) cm^{-1}. This was employed for the next step without further purification.

A stereoisomeric mixture of 6-*hydroxy*-7-m-*chlorobenzoyloxy*-11,12-*dimethoxyabieta*-8,11,13-*triene* (XX). A soln of *m*-chloroperbenzoic acid (85% purity, 207 mg) in CH_2Cl_2 (3 ml) was added to a soln of XIX (312 mg) in CH_2Cl_2 (1 ml). The mixture was left to stand at room temp (10–15°) for 2 days, washed with Na_2CO_3 aq, dried (K_2CO_3) and concentrated *in vacuo* to give 429 mg (92%) of gummy XX, ν_{max} ~3600 (m), 1720 (s), 1600 (w), 1570 (w), 1290 (s), 1250 (s), 1060 (s), 1020 (s), 725 (s) cm^{-1}. This was employed for the next step without further purification.

11,12-*Dimethoxyabieta*-8,11,13-*trien*-6-*one* (XXI). The gummy XX described above was combined with a crude gummy XX obtained from crude oily XVIII. This (1·20 g) was heated at 230–245° on an oil bath for 20 min *in vacuo* (20 mm Hg). During the reaction period, *m*-chlorobenzoic acid gradually sublimed. After cooling, the content of the reaction flask was dissolved in $CHCl_3$. The $CHCl_3$ soln was washed with $NaHCO_3$ aq, dried (K_2CO_3) and concentrated *in vacuo* to give 0·8 g of an oil. This was chromatographed on alumina (Wako Pure Chemicals, ca-300 mesh, 30 g, 13 × 1·8 cm) in light petroleum. Light petroleum (50 ml) eluted 99 mg of unidentified oily hydrocarbon. Light petroleum–ether (9:1, 50 ml) eluted 211 mg of crystalline XVII which was contained as an impurity in the crude XVIII. Further elution with light petroleum–ether (9:1, 150 ml) gave 257 mg of crystalline XXI. Recrystallization from light petroleum gave rhombs, m.p. 113–115°; ν_{max} 1725 (vs), 1605 (w), 1570 (w), 1410 (s), 1390 (vs), 1320 (s), 1230 (s), 1080 (vs), 1045 (s), 1030 (s) cm^{-1}. (Found: C, 76·28; H, 9·32. Calc. for $C_{22}H_{32}O_3$: C, 76·70; H, 9·36%).

11,12-*Dihydroxyabieta*-8,11,13-*trien*-6-*one* (XXII). To a soln of XXI (250 mg) in CH_2Cl_2 (1 ml) cooled in a Dry Ice-acetone bath, there was added slowly a soln of BBr_3 (1 ml) in CH_2Cl_2 (1·5 ml). The intensely purple soln was kept in the cooling bath for 10 min and then removed from the bath. After 30 min at room temp the mixture was concentrated *in vacuo* to remove the solvent and excess reagent, diluted with ice-water and extracted with EtOAc. The extract was washed with $NaHCO_3$ aq and sat NaCl aq, dried ($MgSO_4$) and concentrated *in vacuo* to give 240 mg of semi-solid. This was dissolved in EtOAc (5 ml) and placed on the top of a column of silicic acid (Mallinckrodt AR, 100 mesh, 10 g, 7 × 1·5 cm) in n-hexane. n-Hexane (50 ml) eluted 108 mg of crystalline XXII. Elution with n-hexane–EtOAc (9:1, 150 ml) gave 70 mg of crystalline XXII. The crystalline product (178 mg, 77%) was twice recrystallized from EtOAc–light petroleum to give 93 mg of rhombic crystals, m.p. 168–170°; ν_{max} 3530 (s), 3230 (s), 1685 (vs), 1610 (m), 1500 (s), 1310 (s), 1255 (m), 1235 (m), 1220 (m), 1170 (m), 1060 (m), 990 (m), 850 (m) cm^{-1}; MS (measured with a Hitachi RMU-6L spectrometer): 316 (M^+), 302, 301, 283, 274, 273, 231, 217. (Found: C, 75·90; H, 8·89. Calc. for $C_{20}H_{28}O_3$: C, 75·91; H, 8·92%).

Taxodione (I). Silver oxide (83 mg) was added to a soln of pure XXII (57 mg) in $CHCl_3$ (10 ml) and the mixture was stirred for 2 hr at 50°. After cooling, the brown-colored reaction mixture was poured on to a column of solicic acid (Mallinckrodt AR, 100 mesh, 10 g, 5·5 × 1·6 cm) in $CHCl_3$. Elution with $CHCl_3$ (100 ml) gave 32 mg (56%) of taxodione (I) as golden crystals. Recrystallization from EtOAc–light petroleum gave golden plates, m.p. 108–110°. An authentic sample of taxodione melted at 108–109°. No mp depression was observed upon admixture of synthetic product with the natural product. ν_{max} (CCl_4 soln) 3340 (m), 2960 (s), 2920 (s), 2880 (m), 1684 (vs), 1646 (s), 1630 (vs), 1620 (vs), 1600 (s), 1455 (m), 1420 (s), 1385 (s), 1350 (vs), 1285 (m), 1270 (m), 1240 (w), 1220 (w), ~1170 (w), 1160 (w), 1145 (w), 1138 (s), 1048 (m), 1020 (w), 902 (s) cm^{-1}; ν_{max} (Nujol) 3400 (m), 1660 (vs), 1640 (s), 1615 (vs, doublet), 1600 (s), 1560 (w), 1420 (s), 1360 (vs), 1325 (m), 1310 (w), 1290 (m), 1275 (s), 1245 (s), 1225 (m), 1200 (w), 1170 (m), 1140 (s), 1110 (w), 1090 (w), 1070 (w), 1050 (m), 1020 (m), 990 (m), 975 (m), 970 (m), 902 (vs), 805 (m) cm^{-1}; λ_{max} (EtOH) 321 (ε 20,700), 331 (ε 21,000), 400 (ε 2,500) mμ; MS: 314 (M^+), 299, 287, 286, 272, 271, 245, 232, 231; TLC (Kieselgel G nach Stahl, EtOAc:benzene = 1:9): R_f 0·63. The authentic sample exhibited entirely identical IR, NMR and mass spectra with those of the synthetic product and they were indistinguishable by TLC. (Found: C, 76·34, 76·62; H, 8·61, 8·33. Calc. for $C_{20}H_{26}O_3$: C, 76·40; H, 8·34%).

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