Crystal Structure and Absolute Configuration of a New Sesquiterpenoid Metabolite of *Fomes annosus*, 7α,8β,11-Trihydroxydrimane

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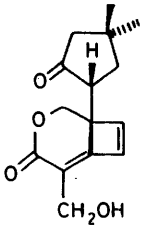
The structure of the title compound, a new metabolite isolated from *Fomes annosus* culture, was established from spectral data, by single-crystal *X*-ray analysis, and by partial synthesis from drimenol.

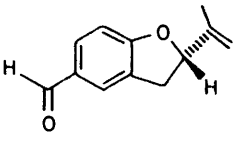
FOMES annosus (syn. *Heterobasidion annosum*, Brief) is considered one of the most destructive of forest pathogens, causing root rot and heart rot of living trees throughout the temperate region. A phytotoxin fomannosin (1) [1] present in the culture broth was claimed to have toxic properties. Recently a second and more active metabolite fomannoxin (2) [2] was isolated from the culture broth and the mycelium and was also found in the decayed wood of a Sitka spruce.[3] In continuation of our search for toxic principles produced in the culture medium of the strain D_4, a new sesquiterpene metabolite was isolated and the structure (3) was assigned.

The new metabolite has the composition $C_{15}H_{28}O_3$ ($M^{+\cdot}$ 256) and the i.r. spectrum showed that it contained hydroxy but no carbonyl functions. The ^1H n.m.r. spectrum revealed the presence of $-CH(CH_2OH)$ and $-CH(OH)CH_2-$ groups as well as four uncoupled methyl groups; no signal occurred in the double-bond region. The u.v. spectrum contained no significant absorption above 210 nm.

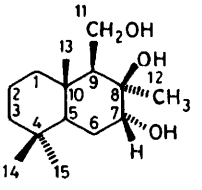
On acetylation of the natural product, a diacetate was formed which still retained a hydroxy-signal in its i.r. spectrum. A primary, secondary, and tertiary group



(1)



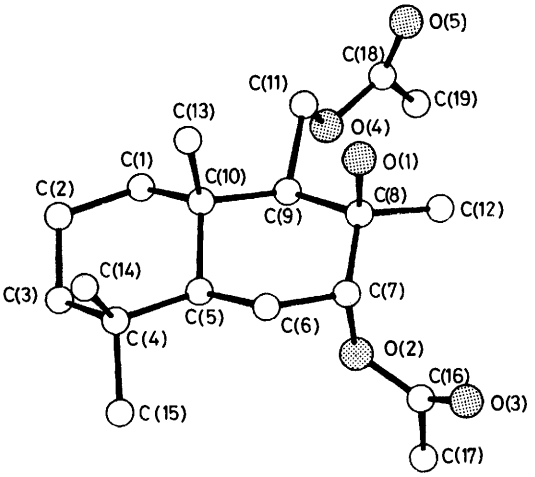
(2)



(3)

in the metabolite would account for the three oxygen functions. As the quantity of material for the structural assignment was small, the crystalline diacetate was subjected to single-crystal *X*-ray analysis.

A view of the molecular conformation is shown in the Figure. The two rings are *trans*-fused and adopt the chair conformation; the distances between the axial substituents C(13), C(14), and O(1) are C(13) · · · C(14) 3.24 Å and C(13) · · · O(1) 2.93 Å. The tertiary hydroxy-group and the secondary acetoxy-group are *trans* diaxial.



Molecular structure of 7α,8β-11-trihydroxydrimane (3)

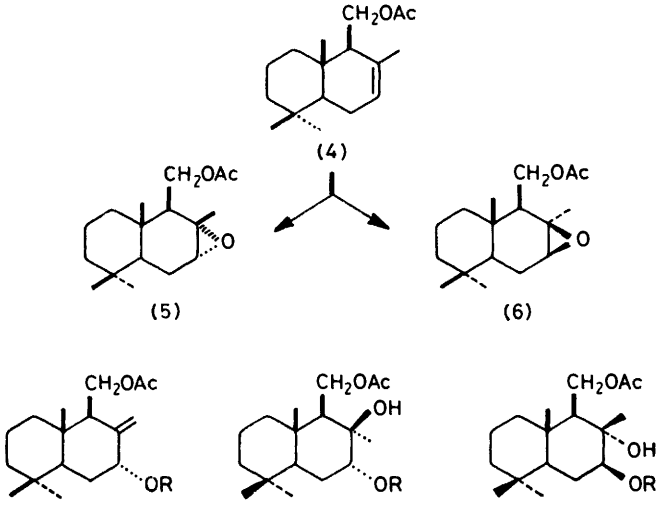
The acetate group at C-11 appears to be disordered (large *B* values) whilst the second acetate group at C-7 is well defined. The oxygen atom O(3) is intermolecularly hydrogen bonded (d = 2.81 Å) to the hydroxy-proton of an adjacent molecule.

The absolute configuration of the trihydroxydrimane remained to be established. A correlation with drimenol of known absolute configuration [4] was carried out (Scheme). Starting with drimenyl acetate (4), epoxidation with *m*-chloroperbenzoic acid in methylene chloride afforded a 91% yield of mixed epoxides which on chromatography gave the known α-epoxide (5) as the major component and the β-epoxide (6) and the minor.[5] Both epoxides were characterized by their n.m.r. spectra.

Trans-diaxial opening of the oxiran ring occurred when the epoxide (5) was treated with aqueous acetic acid. The expected nucleophilic attack at C-8 afforded the *trans*-diaxial alcohol (8a) although in low yield, as it was accompanied by the alcohol (7a) which has an 8-methylene substituent (δ 4.67 and 5.07). Both compounds were characterized by their ^1H n.m.r. spectra

and by those of their acetyl derivatives (7b) and (8b). A second diol (9a) arising by a nucleophilic attack at C-7 was isolated as a minor product. The β-stereochemistry for the secondary hydroxy-group [6] in the diol (9a) is indicated by the value of the $W_{\frac{1}{2}}$ of the ^{1}H n.m.r. signal at δ 3.62.

Similar treatment of the epoxide (6) gave the diol (8a) and its diacetate (8b) as major products together with a trace amount of the diol (9a). These results indicate



SCHEME

that the ring opening of the epoxide (6) occurs predominantly at C-7, which may be due to steric hindrance by the methyl group at C-10.

The diacetate (8b) was identical in all respects (melting point, ^{1}H n.m.r. and mass spectra, $[\alpha]_D$) with the diacetate of the natural product. Since the optimal rotations are the same, the absolute configuration of the natural drimane triol is as shown in structure (3).

The phytotoxic properties of the 7α,8β,11-trihydroxydrimane (3) are under investigation.

EXPERIMENTAL

M.p.s were determined on a Köfler hot stage. ^{1}H N.m.r. spectra were recorded for solutions in deuteriochloroform unless otherwise stated (Me_4Si as internal standard). Optical rotations were obtained for solutions in chloroform. Mass spectra were determined at 70 eV. Preparative and analytical t.l.c. were carried out on $PF_{254+366}$ and GF_{254} silica gel respectively. Organic extracts were dried over sodium sulphate.

Extraction of Fomes annosus *culture medium.*—A modified Raulins medium (4 l) was placed in 16 × 1-l Roux flasks (250 ml of broth per flask) fitted with Morton closures and autoclaved at 120 °C for 20 min. The flasks were each inoculated with 4 × 1 mm plugs of mycelium from an agar plate of *F. annosus* (D_4) and the surface cultures were incubated at 24 °C in the dark. After 42 days the cultures were harvested by filtration and the filtrate was extracted with chloroform (×2). Evaporation of the chloroform yielded an extract (1.52 g) which was separated on a column of silica gel [eluant benzene, chloroform–benzene (1 : 9), chloroform–benzene (1 : 1), chloroform, and acetone–chloroform (1 : 1)]. Appropriate fractions were collected yielding five combinations [(i)—(v)]. Fractions (i) (60 mg) and (iii) (250 mg) are presently under investigation. Fraction (ii) (450 mg) gave (2*S*)-fomannoxin (150 mg). Fraction (iv) (150 mg) on preparative t.l.c. [chloroform–ethyl acetate (1 : 1)] afforded (7*S*,9*R*)-fomannosin (8 mg). A white solid (103 mg) was obtained from fraction (v) (270 mg) which was crystallized from benzene–acetone to give 7α,8β,11-trihydroxydrimane (3) as needles (74 mg), m.p. 152—155°, *m/e* 256 (M^+) $[\alpha]_D$ −25.3° (*c* 0.08), $\nu_{max.}$ (KBr) 3 350 cm^{-1}, δ (CD_3OD) 0.99 (6 H, s, Me-15 and -14), 1.25 (3 H, s, Me-13), 1.45 (3 H, s, Me-12), 3.64 (1 H, dd, *J* 2.6 and 2.8 Hz, 7-H), 4.10 (2 H, 2 × dd, *J* 2.8, 3.2, and 12.0 Hz, 11-H).

7α,11-Diacetoxy-8β-hydroxydrimane.— 7α,8β,11-Trihydroxydrimane (3) (30 mg) was dissolved in pyridine–acetic anhydride [3 ml (1 : 2)] and the solution kept at 20 °C for 16 h. The mixture was added to ice–HCl and extracted with chloroform. The oil, obtained on evaporation of the solvent, was purified by preparative t.l.c. [ethyl acetate–chloroform (1 : 4)] to afford a fraction which crystallized from light petroleum (b.p. 60—80 °C) as needles of 7α,11-diacetoxy-8β-hydroxydrimane (35 mg), m.p. 106—107 °C, *m/e* 340 (M^+), $[\alpha]_D$ −45.32° (*c* 0.12), $\nu_{max.}$ (KBr) 3 475, 1 740, and 1 723 cm^{-1}, δ 0.80, 0.82, and 1.00 (9 H, 3 × s, Me-13, -14, and -15), 1.18 (3 H, s, Me-12), 2.05 and 2.08 (6 H, 2 × s, 2 × OAc), 4.32 (2 H, 2 × dd, *J* 2.9, 4.7, and 12.2 Hz, 11-H), and 4.76 (1 H, dd, *J* 2.7 and 2.9 Hz, 7-H). A sample was crystallized from light petroleum for *X*-ray analysis.

Crystal Data.—$C_{19}H_{32}O_5$, M = 340.5. Monoclinic, a = 10.54(3), b = 9.30(1), c = 10.53(3) Å, β = 105.6(3)°, U = 994.15 Å^3, Z = 2, D_c = 1.14, $F(000)$ = 372. Space group $P2_1$, Mo-K_α radiation (graphite monochromator), λ = 0.7107 Å, μ = 0.87 cm^{-1}.

Intensity data were collected on a Phillips PW 1100 diffractometer using the ω-2θ scan technique. Of the 2 534 reflexions measured, only 750 having $I > 3\sigma(I)$ could be considered as observed. The structure was solved by direct methods with program MULTAN [7] and refined by full-matrix least-squares procedure with isotropic temperature factors. Since the difference Fourier maps suggested the existence of two statistical positions, the disordered acetate group was treated as two rigid groups of equal weight with fixed *B* factors. The refinement was achieved by the program ORION,[8] all the other atoms being kept isotropic. The final *R*-value was 0.13. Final atomic co-ordinates are listed in Table 1, bond lengths in Table 2, and bond angles in Table 3. Structure factors are listed in Supplementary Publication No. SUP 22837.*

Drimenyl Acetate (4).—Drimenol [4] (200 mg) was dissolved in pyridine (2 ml) and acetic anhydride (2 ml) added and the reaction mixture kept at 20 °C for 16 h. The solution was added to ice–HCl and extracted with chloroform. The resultant oil obtained on evaporation of the solvent was purified by preparative t.l.c. (chloroform). The drimenyl acetate was an oil (202 mg), $[\alpha]_D$ +9.7° (*c* 0.68), $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1}, δ 0.83 and 0.89 (9 H, 2 × s, Me-13, -14, and -15), 1.69 (3 H, s, Me-12), 2.06 (3 H, s, OAc), and 4.25 (2 H, 2 × dd, *J* 2.9, 5.7, and 12.0 Hz, 11-H), 5.67 (1 H, m, $W_{\frac{1}{2}}$ 9.0 Hz, 7-H).

* For details of the Supplementary Publications scheme, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1979, Index issue.

11-*Acetoxy*-7α,8- *and* -7β,8-*epoxydriname* (5) *and* (6).—Drimenyl acetate (4) (120 mg) in methylene chloride (20 ml) was cooled to −15 °C, *m*-chloroperbenzoic acid (30 ml) was added slowly, and the mixture kept at −15 °C for 40 h. The solution was worked up to give an oil (110 mg) which later solidified. Purification by preparative t.l.c. [ether–hexane (2 : 3)] yielded two major bands. Band I on elution with chloroform afforded 11-acetoxy-7β,8-epoxydrimane (6) (45 mg) as an oil, $[\alpha]_D$ +37.1° (*c* 0.56), $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1}, δ 0.86 and 0.88 (6 H, 2 × s, Me-15 and -14), 0.92 (3 H, s, Me-13), 1.36 (3 H, s, Me-12), 2.09 (3 H, s, OAc), 3.08 (1 H, d, *J* 6.0 Hz, 7-H), and 4.39 (2 H, 2 × dd, *J* 3.3, 6.6, and 12.0 Hz, 11-H). Band II when eluted with chloroform and evaporated yielded 11-acetoxy-7α,8-epoxydrimane (5) (60 mg), m.p. 54—56 °C (lit.,[5] 55—57 °C), $[\alpha]_D$ +35.1° (*c* 2.26), $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1}, δ 0.83 and 0.88 (9 H, 2 × s, Me-13, -14, and -15), 1.37 (3 H, s, Me-12), 2.11 (3 H, s, OAc), 3.04 (1 H, dd, $W_{\frac{1}{2}}$ 4.6 Hz, 7-H), and 4.35 (2 H, 2 × dd, *J* 4.0, 7.0, and 12.0 Hz, 11-H).

TABLE 1

Atomic co-ordinates (× 10^3), with estimated standard deviations in parentheses, and thermal *B* factors ($Å^2$)

Atom	*x*	*y*	*z*	*B*
C(1)	470(2)	821(0)	1 046(2)	3.6
C(2)	442(3)	797(4)	1 184(3)	5.3
C(3)	353(3)	905(4)	1 211(2)	5.1
C(4)	215(3)	902(4)	1 116(3)	5.6
C(5)	236(2)	920(4)	975(2)	3.9
C(6)	107(2)	919(4)	863(3)	5.0
C(7)	127(3)	965(4)	734(3)	4.3
C(8)	231(3)	884(4)	690(3)	5.7
C(9)	360(2)	868(4)	808(2)	3.5
C(10)	340(2)	811(4)	943(2)	3.6
C(11)	459(3)	773(4)	754(3)	6.5
C(12)	257(3)	951(4)	565(3)	4.6
C(13)	291(2)	651(3)	928(2)	4.1
C(14)	138(2)	764(4)	1 138(3)	5.2
C(15)	136(3)	1 036(5)	1 143(3)	7.9
O(1)	177(2)	743(3)	658(2)	6.0
O(2)	169(2)	1 118(3)	753(2)	4.4
C(16)	101(3)	1 210(4)	667(3)	5.0
C(17)	160(3)	1 366(4)	698(3)	7.0
O(3)	2(2)	1 187(3)	585(2)	7.2
O(4)	537(4)	881(5)	739(5)	7.5
C(18)	580(4)	852(5)	635(5)	8.5
C(19)	661(4)	983(5)	606(5)	10.0
O(5)	555(4)	747(5)	568(5)	10.0
O(4′)	576(4)	898(5)	721(5)	7.5
C(18′)	635(4)	880(5)	625(5)	8.5
C(19′)	596(4)	731(5)	558(5)	10.0
O(5′)	711(4)	962(5)	599(5)	10.0

Action of Acetic Acid on 11-*Acetoxy*-7α,8-*epoxydrimane* (5).—11-Acetoxy-7α,8-epoxydrimane (5) (60 mg) in acetic acid (2 ml) and water (2 ml) was stirred for 48 h. The reaction mixture was diluted with water and extracted with ethyl acetate. An oil (53 mg), obtained on work-up, was separated by preparative t.l.c. [ethyl acetate–chloroform (3 : 20)] into four bands. Band I (14 mg) was a mixture which after further preparative t.l.c. (7% v/v ethyl acetate–chloroform) gave a solid (2 mg) which was not identified, m.p. 137—141 °C, $[\alpha]_D$ +16.5°.

Band II on elution with ethyl acetate and evaporation afforded 1β-*acetoxymethyl*-2-*methylene*-5,5,10β-*trimethyl*-trans-*decal*-3α-*ol* (7a) (9 mg) which was crystallized from light petroleum (b.p. 60—80 °C) to give needles m.p. 98—99 °C (Found: C, 72.4; H, 10.35. $C_{17}H_{28}O_3$ requires C, 72.8; H, 10.05%), *m/e* 280 (M^+), $[\alpha]_D$ −38.8° (*c* 0.44), $\nu_{max.}$ (KBr) 3 545 and 1 720 cm^{-1}, δ 0.74, 0.82, and 0.92 (9 H, 3 × s, Me-5, -5, and -10), 2.02 (3 H, s, OAc), 2.55 (1 H, m, $W_{\frac{1}{2}}$ 13.0 Hz, 1-H), 4.26 (2 H, 2 × dd, *J* 4.9, 8.2, and 11.1 Hz, $-CH_2-$), 4.38 (1 H, m, $W_{\frac{1}{2}}$ 5.0 Hz, 3-H), and 4.67 and 5.07 (2 H, 2 × m, $W_{\frac{1}{2}}$ 5.0 and 3.5 Hz, $=CH_2$). The alcohol (7a) (5 mg) was dissolved in pyridine (0.5 ml), acetic anhydride (1.0 ml) was added and the solution was kept at 20 °C for 16 h. The mixture was poured into ice–HCl and extracted with ethyl acetate to yield 3α-acetoxy-1β-acetoxymethyl-2-methylene-5,5,10β-trimethyl-*trans*-decalin (7b) (5 mg) as an oil, *m/e* 322 (M^+), $[\alpha]_D$ −17.2° (*c* 0.41), $\nu_{max.}$ ($CHCl_3$) 1 728 cm^{-1} δ 0.77, 0.81, and 0.84 (9 H, 3 × s, Me-5, -5, and -10), 2.02 and 2.06 (6 H, 2 × s, 2 × OAc), 2.42 (1 H, m, $W_{\frac{1}{2}}$ 16.0 Hz, 1-H), 4.26 (2 H, 2 × dd, *J* 4.6, 8.3, and 11.2 Hz, $-CH_2-$), 4.78 and 5.19 (2 H, d, and s, *J* 1.3 Hz $=CH_2$), and 5.43 (1 H, dd, *J* 2.0 and 2.4 Hz, 3-H).

TABLE 2

Bond lengths (Å) (distances between statistical atoms appear with an asterisk)

C(1)–C(2)	1.58(4)	O(2)–C(16)	1.32(4)
C(1)–C(10)	1.51(3)	C(16)–C(17)	1.58(5)
C(2)–C(3)	1.45(5)	C(16)–O(3)	1.19(4)
C(3)–C(4)	1.53(4)	O(4)–C(18)	1.33(6)
C(4)–C(5)	1.57(4)	O(4) · · · O(4′)	0.53(6) *
C(4)–C(14)	1.57(5)		
C(4)–C(15)	1.57(5)	C(18)–C(19)	1.56 (6)
C(5)–C(6)	1.55(4)	C(18)–O(5)	1.19(7)
C(5)–C(10)	1.59(4)	C(18)–O(4′)	
C(6)–C(7)	1.50(4)	C(18) · · · C(18′)	0.66(6) *
C(7)–C(8)	1.50(4)		
C(7)–O(2)	1.48(4)		
C(8)–C(9)	1.59(4)		
C(8)–C(12)	1.55(4)	C(19) · · · O(5′)	0.58(6) *
C(8)–O(1)	1.44(5)		
C(9)–C(10)	1.60(4)	O(5) · · · C(19′)	0.50(6) *
C(9)–C(11)	1.58(4)	O(4′)–C(18′)	1.33(4)
C(10)–C(13)	1.57(5)	C(18′)–C(19′)	1.56(1)
C(11)–O(4)	1.33(6)	C(18′)–O(5′)	1.19(5)
C(11)–O(4′)	1.80(5)		

Band III on elution with ethyl acetate and evaporation afforded a solid (10 mg) which was crystallized from light petroleum (b.p. 60—80 °C) to give needles of 11-acetoxy-7β,8α-dihydroxydrimane (9a), *m/e* 298 (M^+), $[\alpha]_D$ −53.7° (*c* 0.18), $\nu_{max.}$ (KBr) 3 400 and 1 735 cm^{-1}, δ 0.80, 0.86, and 0.89 (9 H, 3 × s, Me-13, -14, and -15), 1.16 (3 H, s, Me-12), 1.55 and 2.89 (2 H, 2 × s, exchangeable with D_2O, 2 × OH),

TABLE 3

Bond angles (°) (mean standard deviation, 3°)

C(2)–C(1)–C(10)	107	C(9)–C(8)–O(1)	107
C(1)–C(2)–C(3)	112	C(12)–C(8)–O(1)	108
C(2)–C(3)–C(4)	114	C(8)–C(9)–C(10)	116
C(3)–C(4)–C(5)	106	C(8)–C(9)–C(11)	106
C(3)–C(4)–C(14)	111	C(10)–C(9)–C(11)	113
C(3)–C(4)–C(15)	109	C(1)–C(10)–C(5)	111
C(5)–C(4)–C(14)	116	C(1)–C(10)–C(9)	108
C(5)–C(4)–C(15)	107	C(1)–C(10)–C(13)	110
C(14)–C(4)–C(15)	108	C(5)–C(10)–C(9)	104
C(4)–C(5)–C(6)	114	C(5)–C(10)–C(13)	114
C(4)–C(5)–C(10)	114	C(9)–C(10)–C(13)	110
C(6)–C(5)–C(10)	110	C(9)–C(11)–O(4)	96
C(5)–C(6)–C(7)	113	C(7)–O(2)–C(16)	116
C(6)–C(7)–C(8)	115	O(2)–C(16)–C(17)	110
C(6)–C(7)–O(2)	105	O(2)–C(16)–O(3)	127
C(8)–C(7)–O(2)	108	C(17)–C(16)–O(3)	123
C(7)–C(8)–C(9)	110	C(11)–O(4)–C(18)	108
C(7)–C(8)–C(12)	112	O(4)–C(18)–C(19)	110
C(7)–C(8)–O(1)	105	O(4)–C(18)–O(5)	125
C(9)–C(8)–C(12)	113	C(19)–C(18)–O(5)	125
		C(9)–C(11)–O(4′)	105

2.06 (3 H, s, OAc), 3.63 (1 H, m, $W_{\frac{1}{2}}$ 9.3 Hz, 7-H), 4.28 (2 H, 2 × dd, J 3.9, 5.5, and 12.0 Hz, 11-H). 11-Acetoxy-7β,8α-dihydroxydrimane (9a) (5 mg) was dissolved in pyridine (0.5 ml), acetic anhydride (1.0 ml) was added, and the solution was kept at 20 °C for 16 h. The reaction mixture was poured into ice–HCl and extracted with ethyl acetate to give 7β,11-diacetoxy-8α-hydroxydrimane (9b) as an oil (4 mg), $[\alpha]_D$ −91.1° (*c* 0.09), $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1}, δ 0.79 and 0.89 (9 H, 2 × s, Me-13, -14, and -15), 1.17 (3 H, s, Me-12), 1.55 (1 H, s, exchangeable with D_2O, 8-OH), 2.04 and 2.12 (6 H, 2 × s, 2 × OAc), 4.30 (2 H, 2 × dd, 2.7, 5.8, and 11.7 Hz, 11-H), and 4.81 (1 H, 7-H).

Band IV on elution with ethyl acetate and evaporation yielded a solid (9 mg) which was crystallized from light petroleum (b.p. 60—80 °C) to give needles of 11-*acetoxy*-7α,8β-*dihydroxydrimane* (8a), m.p. 146—147 °C (Found: C, 68.3; H, 10.4. $C_{17}H_{30}O_4$ requires C, 68.42; H, 10.13%), $[\alpha]_D$ −4.1° (*c* 0.58), $\nu_{max.}$ (KBr) 3 485 and 1 725 cm^{-1}, δ 0.84, 0.88, and 1.01 (9 H, 3 × s, Me-13, -14 and -15), 1.27 (3 H, s, Me-12), 1.57 and 1.70 (2 H, 2 × s, exchangeable with D_2O, 7α- and 8β-OH), 3.62 (1 H, m, $W_{\frac{1}{2}}$ 7.6 Hz, 7-H), 4.33 (2 H, 2 × dd, J 3.2, 4,4, and 12.2 Hz, 11-H). 11-Acetoxy-7α,8β-dihydroxydrimane (8a) (10 mg) was dissolved in pyridine (0.5 ml), acetic anhydride was added, and the solution was kept at 20 °C for 16 h. The reaction mixture was poured into ice–HCl and extracted with ethyl acetate which was worked up to give an oil (9 mg). Addition of light petroleum (b.p. 60—80 °C) afforded needles of 7α,11-diacetoxy-8β-hydroxydrimane (8b), $M^{+\cdot}$ 340, m.p. and mixed m.p. (with the diacetate of the natural product) 106—107 °C, $[\alpha]_D$ −44.4°. The spectra were identical with those of the diacetate of the natural product.

Action of Acetic Acid on 11-*Acetoxy*-7β,8-*epoxydrimane* (6). —11-Acetoxy-7β,8-epoxydrimane (6) (45 mg) was stirred in acetic acid–water [4 ml (1 : 1)] for 48 h. The mixture was then diluted with water and extracted with ethyl acetate to give an oil (35 mg). The oil was separated by preparative t.l.c. [ethyl acetate–chloroform (3 : 20)] and was found to have four components. Band I (7 mg) was a mixture and was not investigated further. Band II (3 mg) on elution with ethyl acetate and evaporation yielded a solid which was crystallized from light petroleum (b.p. 60—80 °C) to give needles of 7α,11-diacetoxy-8β-hydroxydrimane (8b), m.p. 106—107.5 °C. Band III (trace) was identified (t.l.c.) as 11-acetoxy-7β,8α-dihydroxydrimane (9a). Band IV (19 mg), on elution with ethyl acetate and evaporation, afforded a solid which crystallized from light petroleum (b.p. 60—80 °C) as needles of 11-acetoxy-7α,8β-dihydroxydrimane (8a), m.p. 146—147 °C.

We thank the Director, Institute for Industrial Research and Standards, and the Forest and Wild Life Service, Department of Fisheries and Forestry, for financial support. We are grateful to Professor K. Overton for a generous gift of drimenol.

[9/1839 *Received*, 19*th November*, 1979]

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