Structure and Absolute Configuration of (−)-Taylorione, a Novel Carbon Skeletal Sesquiterpene Ketone of *ent*-1,10-seco-Aromadendrane Form, from *Mylia taylorii* (Liverwort)

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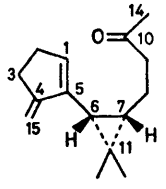
The structure and absolute configuration of (−)-taylorione, isolated from the liverwort, *Mylia taylorii*, was elucidated to be *ent*-1,10-seco-aromadendra-1(5),4(15)-dien-10-one (1) on the basis of chemical and spectral evidence.

LIVERWORTS contain characteristic oil bodies in each cell of the gametophytes which grow from the spores and form the usual plant bodies. In the course of our investigation on terpenoids of the liverworts, several new sesquiterpenoids have been isolated, almost all of which were enantiomers of those obtained from higher plants.[1] From a leafy liverwort, *Mylia taylorii* (Hock.) Gray belonging to the *Jungermanniaceae*, a sesquiterpene ketone, named (−)-taylorione (1), was isolated.[2] This



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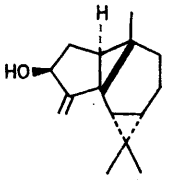

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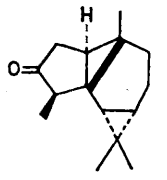
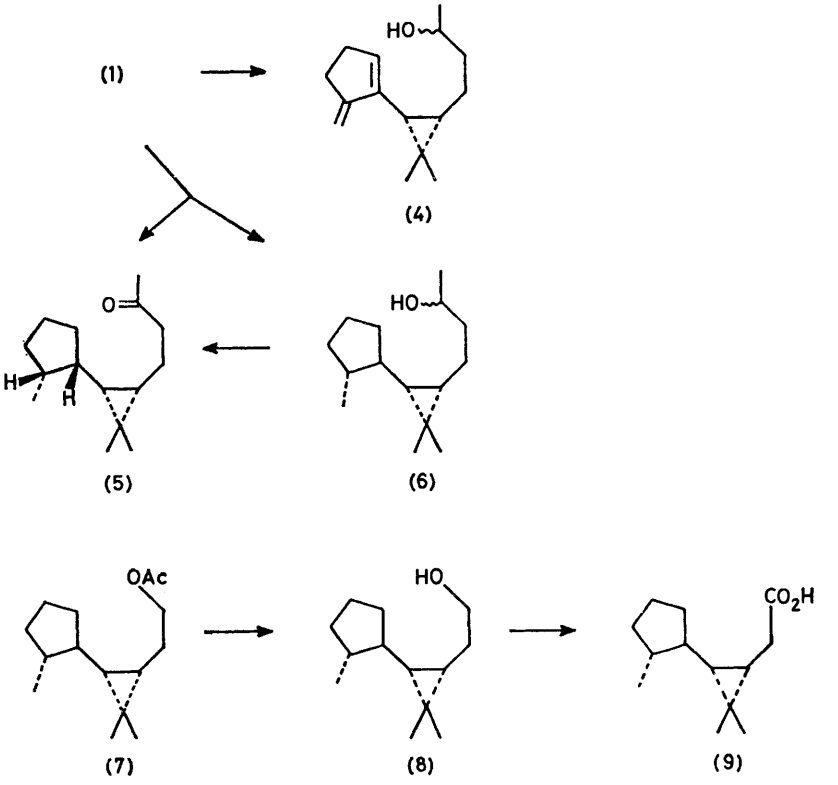


(3)

ketone, containing a novel carbon skeleton, has now been shown to be *ent*-1,10-seco-aromadendra-1(5),4(15)-dien-10-one (1). This paper deals with the chemical and spectral evidence for the proposed absolute configuration (1).

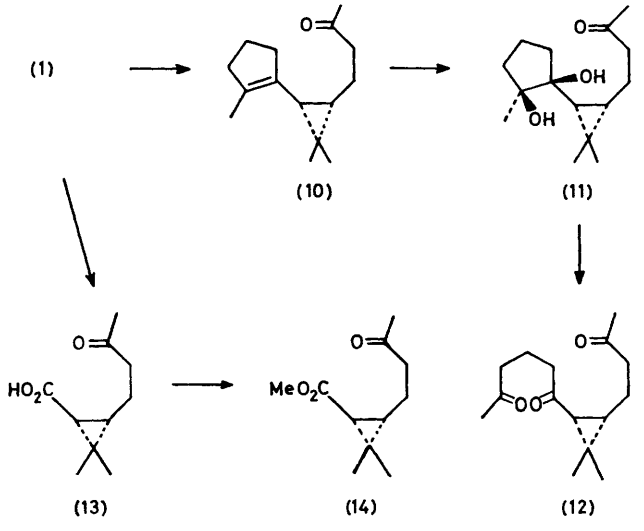
(−)-Taylorione (1), $C_{15}H_{22}O$, $[\alpha]_D$ −28.1°, a colourless oil, was isolated from a hexane extract of the liverwort by column and preparative thin layer chromatography over silica gel. (−)-Myliol (2) and (−)-dihydromylione A (3), whose structures have been previously determined,[3,4] were also isolated together with a hydrocarbon fraction, from which three known sesquiterpenes, longifolene, β-pompene (gymnomitrene), and bazzanene, were separated by preparative g.l.c.

The i.r. and ^1H n.m.r. spectra of the ketone (1) suggested that it contained a geminal dimethyl group [$\nu_{max.}$ 1 379 and 1 363 cm^{-1}; δ 0.90 and 1.15 (each 3 H, s)], an acetyl group [$\nu_{max.}$ 1 726 cm^{-1}; δ 2.06 (3 H, s)], an exo-methylene [$\nu_{max.}$ 1 634 and 868 cm^{-1}; δ 4.66 and 4.75 (each 1 H, br s)], a trisubstituted double bond [$\nu_{max.}$ 854 cm^{-1}; δ 5.85 (1 H, br s)], and three methylenes [$\nu_{max.}$ 1 430 and 1 415 cm^{-1}; δ 2.3—2.6 (6 H)] adjacent to C=C and/or C=O. The exo-methylene and the trisubstituted double bond were certainly conjugated with



each other since the u.v. spectra of both (−)-taylorione and the alcohol (4), $C_{15}H_{24}O$; $\nu_{max.}$ 3 620 and 3 400 cm^{-1}, obtained by $LiAlH_4$ reduction of the ketone (1), exhibited absorptions [(1), $\lambda_{max.}$ 243 nm (ε 14 900); (4), $\lambda_{max.}$ 243 nm (ε 6 700)] due to a conjugated diene system. When the ketone (1) was hydrogenated over PtO_2 in acetic acid, it furnished a saturated ketone (5), $C_{15}H_{26}O$, $\nu_{max.}$ 1 720 cm^{-1}, and a saturated alcohol (6), $C_{15}H_{28}O$, $\nu_{max.}$ 3 615 and 3 320 cm^{-1}, which was oxidized by Jones reagent to produce the former. The ^1H n.m.r. spectra of the products (5) and (6) showed the presence of two cyclopropane protons (δ 0.42 and 0.40, each 2 H). Thus, taylorione (1) was a bicyclic sesquiterpene ketone containing a cyclopropane ring, a geminal dimethyl grouping, an acetyl group, and a conjugated diene system consisting of an exo-methylene and a trisubstituted double bond.

In tetrahydrotaylorione (5), the acetyl group was deduced to be connected to a saturated carbon chain since the methylene ($\nu_{max.}$ 1 420 cm^{-1}) adjacent to the carbonyl group appeared as a triplet (J 8.0 Hz) at δ 2.40 in the ^1H n.m.r. spectrum. The length of this connecting carbon chain was determined by submitting the ketone (5) to the following degradation reactions. First, Baeyer–Villiger oxidation of the saturated ketone (5) with CF_3CO_3H yielded an ester (7), $\nu_{max.}$ 1 740 cm^{-1}, which was hydrolysed with KOH to give a bis-nor-primary alcohol (8), $C_{13}H_{24}O$, $\nu_{max.}$ 3 630, 3 330, and 1 050 cm^{-1}. The alcohol (8) was then converted into a corresponding acid (9), $C_{13}H_{22}O_2$, $\nu_{max.}$ 3 400—2 500 and 1 710 cm^{-1}, by Jones oxidation. Since the carbinyl methylene of the bis-nor-alcohol (8) showed a triplet (J 7.0 Hz) at δ 3.56 (2 H) and the carboxy-methylene ($\nu_{max.}$ 1 410 cm^{-1}) of the acid (9) a doublet (J 7.0 Hz) at δ 2.29 (2 H), the acetyl group in the original tetrahydrotaylorione (5) should be connected to the cyclopropane ring by two methylene units.



Alternatively, taylorione (1) absorbed one molar equivalent of hydrogen, on catalytic hydrogenation over Pd–C in ethanol, to give a dihydro-ketone (10), $C_{15}H_{24}O$, $\nu_{max.}$ 1 725 and 1 415 cm^{-1}, which contained a newly formed tetrasubstituted double bond bearing a methyl group [δ 1.67 (3 H, br s)]; the formation of such a vinylic methyl grouping was explained by 1,4-addition of hydrogen to the conjugated diene system of the taylorione molecule. The position of the u.v. absorption maximum [λ 212 nm (ε 5 900)] suggested that the tetrasubstituted double bond was in conjugation with the cyclopropane ring.[5] The dihydro-ketone (10) was then oxidized with OsO_4 to give a glycol (11), $C_{15}H_{26}O_3$, $\nu_{max.}$ 3 500, 1 723, and 1 410 cm^{-1}, which, by means of glycol fission with $NaIO_4$, was converted into a triketone (12), $C_{15}H_{24}O_3$. The triketone (12) thus obtained possessed a ketone group conjugated to a cyclopropane ring [$\lambda_{max.}$ (iso-octane) 203 nm (ε 3 000), $\nu_{max.}$ 1 695 cm^{-1}, δ 0.9—1.4 (2 H)][6] and two acetyl groups [$\nu_{max.}$ 1 725 cm^{-1}, δ 2.08 (6 H, s)] together with a geminal dimethyl [$\nu_{max.}$ 1 390, 1 385, and 1 365 cm^{-1}, δ 1.16 (6 H, s)], three methylenes [$\nu_{max.}$ 1 420 cm^{-1}, δ 2.1—2.6 (6 H)] adjacent to the carbonyl group, and two normal methylenes [$\nu_{max.}$ 1 450 cm^{-1}, δ 1.5—2.0 (4 H)].

From the above chemical evidence, the gross structure of taylorione was deduced to be 1,10-seco-aromadendra-1(5),4(15)-dien-10-one (1). This gross structure was also supported by its ^{13}C n.m.r. spectrum which contained four singlets, three doublets, five triplets, and three quartets, assigned as in Table 1. Furthermore, when the ^1H n.m.r. spectrum of (1) was determined in the presence of 0.91 mol of the lanthanide shift reagent $Eu(fod)_3$, a spectrum was obtained in which all the proton signals were completely separated over the range δ 2—11.5. Thus, assignments of the proton signals (Table 2) were performed by coupling pattern analysis, and were supported by the following decoupling experiments. Irradiation at the centre of the triplet (δ 11.03), assigned to the methylene (9-H_2) adjacent to the carbonyl group, re-formed the double triplets of doublets (ddt) at δ 8.05 (8-Ha) and the triple doublets of doublets (dtd) at δ 8.56 (8-Hb) uniformly into double doublets

TABLE 1

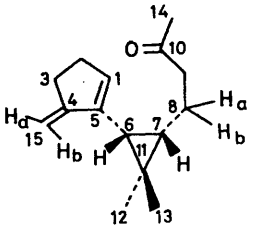
^{13}C N.m.r. spectrum of (−)-taylorione (1) [a]

Carbon assigned	Chemical shift	Multiplicity
1	135.7	d
2	30.5 [b]	t
3	29.2 [b]	t
4	156.8	s
5	141.5	s
6	27.7	d
7	24.5	d
8	20.6	t
9	44.4	t
10	209.0	s
11	18.8	s
12	29.2	q
13	15.8	q
14	29.2	q
15	100.2	t

[a] The ^{13}C n.m.r. spectrum was obtained for a $CDCl_3$ solution with a JEOL LNM-PFT-100 spectrometer (25.15 MHz, pulse repetition 3 s, accumulation 1 800 times, and frequency range 6.25 KHz); chemical shifts were expressed as δ values (p.p.m.) from internal Me_4Si. [b] Assignments may be interchanged.

TABLE 2

^{1}H N.m.r. spectrum of (−)-taylorione (1) [a]



Proton assigned	Chemical shift	Multiplicity and J value
1-H	7.44	br s
2-H_2	3.00 [b]	complex
3-H_2	2.75 [b]	complex
6-H	2.45	d, J_{6-7} 8.0 Hz
7-H	4.68	ddd, J_{7-6} 8.0, J_{7-8a} 8.0, and J_{7-8b} 6.0 Hz
8-H_a	8.05	ddt, J_{8a-8b} 14.0, J_{8a-7} 8.0, and J_{8b-9} 7.0 Hz
8-H_b	8.56	dtd, J_{8b-8a} 14.0, J_{8b-9} 7.0, and J_{8b-7} 6.0 Hz
9-H_2	11.03	t, J_{9-8} 7.0 Hz
12-H_3	2.54	s
13-H_3	2.15	s
14-H_3	11.17	s
15-H_a	5.87	br s
15-H_b	5.35	br s

[a] The ^{1}H n.m.r. spectrum was determined on a Hitachi R22 spectrometer (90 MHz) for a solution in $CDCl_3$ containing 0.91 mol of Eu(fod)$_3$; chemical shifts are expressed as δ values (p.p.m.) from internal Me_4Si. [b] Assignments may be interchanged.

(J 14.0 and 8.0 Hz, J 14.0 and 6.0 Hz). Moreover, irradiation at the frequency of 7-H (δ 4.68) resulted in loss of the couplings (J_{6-7} 8.0, J_{8a-7} 8.0, and J_{8b-7} 6.0 Hz) reforming the 6-H doublet (δ 2.45), the 8-Ha ddt, and the 8-Hb dtd into a singlet and two double triplets, respectively. In confirmation, the decoupling at the 6-H doublet changed the 7-H double doublets of doublets (ddd) to double doublets (J 8.0 and 6.0 Hz). The results of these decoupling experiments revealed the cyclopropane ring to be *cis*-substituted in (−)-taylorione (1).

To confirm the structure and further to elucidate the absolute configuration of (−)-taylorione, the ketone (1) was submitted to ozonolysis in ethyl acetate at −15 °C and the resulting ozonide was oxidatively decomposed with H_2O_2 to afford an acid (13), $C_{10}H_{16}O_3$, $\nu_{max.}$ 3 500—2 500, 1 720, and 1 695 cm^{-1}, which was then converted into a methyl ester (14), $C_{11}H_{18}O_3$, $[\alpha]_D$ −25.1°; $\nu_{max.}$ 1 720 cm^{-1}. The ester was identified as (−)-*cis*-1-methoxycarbonyl-2,2-dimethyl-3-(3-oxo-n-butyl)cyclopropane (14) by comparison of its i.r., ^{1}H n.m.r., and mass spectra with those of the enantiomer, prepared by degradation of (+)-car-2-ene [7] and (+)-bicyclogermacrene.[8]

The structure and absolute configuration of (−)-taylorione was, therefore, elucidated as *ent*-1,10-seco-aromadendra-1(5),4(15)-dien-10-one (1). This unique sesquiterpene ketone (1), as well as (−)-myliol (2) and (−)-dihydromylione A (3), is an addition to the naturally occurring enantiomeric sesquiterpenoids, and the novel carbon skeleton may be biosynthesized from *ent*-aromadendrane precursor *via* oxidative cleavage of the C_1–C_{10} bond. This is very interesting from the viewpoint of sesquiterpenoid biogenesis and chemosystematics.

EXPERIMENTAL

I.r. spectra were recorded on a Hitachi EPI-G3 grating spectrophotometer for solutions in CCl_4 and ^{1}H n.m.r. spectra were measured with Hitachi R20 and Varian T60 instruments, unless otherwise stated, for solutions in CCl_4 with Me_4Si as internal reference. Optical rotations were obtained on a Yanaco OR-50 automatic polarimeter for $CHCl_3$ solutions at room temperature and u.v. spectra were recorded for EtOH solutions with a Hitachi 124 spectrometer. Low-resolution mass spectra were determined at 70 eV on a Hitachi RMS-4 spectrometer, and high resolution mass spectra were taken on a Hitachi RMU-7L double-focusing instrument, equipped with a computer system. All compounds were oils but their homogeneity was established by g.l.c. (columns: SE-30, PEG 20M, and DEGS), t.l.c., and ^{1}H n.m.r. spectroscopy.

Isolation of (−)-*Taylorione* (1).—The liverwort, *Mylia taylorii*, was collected in a forest in Kochi Prefecture. The whole plant (4.4 kg), after being dried in the shade for several days, was digested with hexane at room temperature and the solvent was removed *in vacuo* to obtain a brown viscous substance (11.0 g). The extract (10.0 g) was chromatographed through a silica gel column with hexane–ethyl acetate (6 : 1) to isolate (−)-taylorione (1) (1.40 g) along with (−)-myliol (2) (0.35 g), (−)-dihydromylione A (3) (0.05 g), and a hydrocarbon fraction (0.75 g) which was then applied to preparative g.l.c. (PEG 20M; 10% on Chromosorb AW) to isolate longifolene, β-pompene,[9,10] and bazzanene.[11] Preparative t.l.c. on silica gel (hexane–ethyl acetate, 6 : 1) afforded pure (−)-taylorione (Found: M^+, 218.168 5. $C_{15}H_{22}O$ requires M, 218.166 9); $[\alpha]_D$ −28.1° (*c* 1.52); *m/e* 218, 175, 160, 145, 105, 91, 55, and 43; $\nu_{max.}$ 3 085, 1 726, 1 634, 1 430, 1 415, 1 379, 1 363, 1 164, 868, and 854 cm^{-1}; δ 0.90, 1.15, and 2.06 (each 3 H, s), 4.66 and 4.75 (each 1 H, br s), and 5.85 (1 H, br); $\lambda_{max.}$ 243 nm (ε 14 900).

Lithium Aluminium Hydride Reduction of (−)-*Taylorione* (1).—The ketone (1) (80 mg) was refluxed with $LiAlH_4$ (50 mg) in dry ether (20 ml) for 2 h. The excess of hydride was decomposed by addition of ice–water. Extraction with ether, drying (Na_2SO_4), and evaporation at reduced pressure afforded an oily residue which was purified by preparative t.l.c. to yield the alcohol (4) (70 mg); *m/e* 220 (M^+), 202, 181, 177, 162, 147, 131, 119, 105, 91, 79, 55, and 43; $\nu_{max.}$ 3 620, 3 400, 3 080, 1 645, 1 395, 1 385, 1 130, and 865 cm^{-1}; δ 0.83 and 1.14 (each 3 H, s), 1.10 (3 H, d, J 6.0 Hz), 3.60 (1 H, m), 4.66 and 4.76 (each 1 H, br s), and 5.87 (1 H, br); $\lambda_{max.}$ 243 nm (ε 6 700).

Hydrogenation of (−)-*Taylorione* (1).—Adams catalyst (50 mg) was added to a solution of the ketone (1) (450 mg) in acetic acid (7 ml) and the mixture hydrogenated at room temperature. The catalyst was filtered off, and the filtrate, after being diluted with water, was repeatedly extracted with ether. The solution was washed with 5% w/v $NaHCO_3$–water and then with water, dried over Na_2SO_4, and evaporated. The hydrogenated product thus obtained showed two spots on t.l.c. and the two compounds were isolated by column chromatography. (−)-Tetrahydro-

taylorione (5) (150 mg), $C_{15}H_{26}O$, had M^+ 222; $[\alpha]_D$ −22.3° (*c* 2.88); *m/e* 222, 164, 149, 139, 126, 108, 81, 69, 55, and 43; $\nu_{max.}$ 1 720, 1 420, 1 395, 1 383, 1 367, and 1 170 cm^{-1}; δ 0.42 (2 H, m), 0.90 (3 H, d, *J* 8.0 Hz), 0.94, 1.02, and 2.03 (each 3 H, s), and 2.40 (2 H, t, *J* 8.0 Hz). The saturated alcohol (**6**) (150 mg), $C_{15}H_{28}O$, had M^+ 224; $[\alpha]_D$ −31.2° (*c* 1.35); *m/e* 224, 163, 151, 128, 123, 110, 95, 81, 69, 55, and 43; $\nu_{max.}$ 3 615, 3 320, 1 395, 1 382, and 1 130 cm^{-1}; δ 0.40 (2 H, m), 0.90 (3 H, d, *J* 7.0 Hz), 0.97 and 1.02 (each 3 H, s), 1.14 (3 H, d, *J* 8.0 Hz), and 3.70 (1 H, m).

Baeyer–Villiger Oxidation of (−)-*Tetrahydrotaylorione* (5).—A solution of CF_3CO_3H was prepared by dropwise addition of a solution of $(CF_3CO)_2O$ (0.6 g) in dichloromethane (1 ml) to a suspension of 60% H_2O_2 (250 mg) in dichloromethane (0.5 ml) with stirring in an ice-bath. This solution was added dropwise to a stirred suspension of $NaHSO_4$ (1.0 g) and tetrahydrotaylorione (5) (140 mg) in dichloromethane (2.5 ml) over 15 min. The mixture was further stirred for 1 h and then left for 3 days at room temperature. The mixture was filtered and the insoluble salts were washed with dichloromethane. The combined filtrate was washed with aqueous $NaHSO_3$, water, further aqueous $NaHCO_3$, and water, dried (Na_2SO_4), and evaporated, to afford the product (7) (150 mg), $\nu_{max.}$ 1 740, 1 385, 1 375, 1 360, 1 240, 1 118, and 1 032 cm^{-1}.

Hydrolysis of the Acetate (7).—A mixture of the crude ester (7) (150 mg) in methanol (5 ml) and KOH (0.4 g) in water (2 ml) was refluxed for 2 h on a steam-bath and then the solvent was evaporated off *in vacuo*. The residue was dissolved in water and extracted with ether. The extract was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated, leaving the crude product which was purified by preparative t.l.c. to obtain the bis-nor-alcohol (8) (40 mg), $C_{13}H_{24}O$, M^+ 196; $[\alpha]_D$ −23.6° (*c* 0.79); *m/e* 196, 153, 135, 107, 95, 81, 67, 55, and 43; $\nu_{max.}$ 3 630, 3 330, 1 385, 1 375, and 1 050 cm^{-1}; δ 0.40 (2 H, m), 0.92 (3 H, d, *J* 7.0 Hz), 0.97 and 1.04 (each 3 H, s), and 3.56 (2 H, t, *J* 7.0 Hz).

Jones Oxidation of the Bis-nor-alcohol (8).—Jones reagent (0.6 ml) was added with stirring to a solution of the alcohol (8) (30 mg) in acetone (1.5 ml) in an ice-bath during 1 min and the mixture stirred for 4 min at room temperature. The mixture was poured into ice–water, extracted with ether, and purified by preparative t.l.c. to give the acid (9) (17 mg), $C_{13}H_{22}O_2$, M^+ 210; $[\alpha]_D$ −40.6° (*c* 0.32); *m/e* 210, 167, 150, 128, 96, 81, 67, 55, and 43; $\nu_{max.}$ 3 400—2 500, 1 710, 1 410, 1 385, and 1 375 cm^{-1}; δ 0.93 (3 H, d, *J* 7.0 Hz), 1.00 and 1.11 (each 3 H, s), 2.29 (2 H, d, *J* 7.0 Hz), and 10.20 (1 H, br).

Selective Hydrogenation of (−)-*Taylorione* (1).—The ketone (1) (360 mg) was hydrogenated over 5% Pd–C (25 mg) in ethanol (10 ml). When *ca.* 1 mol. equiv. of hydrogen had been taken up, the reaction was stopped. The mixture was filtered, and the filtrate concentrated *in vacuo* to obtain a crude product which was chromatographed on silica gel to give the dihydro-ketone (10) (320 mg) as a light yellow oil, $C_{15}H_{24}O$, M^+ 220; $[\alpha]_D$ −25.0° (*c* 0.88); *m/e* 220, 177, 162, 149, 121, 107, 55, and 43; $\nu_{max.}$ 1 725, 1 415, 1 390, 1 380, and 1 363 cm^{-1}; δ 0.93 and 1.12 (each 3 H, s), 1 67 (3 H, br s), and 2.03 (3 H, s); $\lambda_{max.}$ 212 nm (ε 5 900).

Oxidation of (−)-*Dihydrotaylorione* (10) *with Osmium Tetraoxide*.—A solution of OsO_4 (210 mg) in dry benzene (3 ml) was added to a solution of the ketone (10) (180 mg) in dry benzene (8 ml) and dry pyridine (0.8 ml), and the mixture left at room temperature for 6 days. The benzene was evaporated off and the residue dissolved in ethanol (15 ml). The solution was added to a solution of Na_2SO_3 (1.7 g) in water and the mixture heated under reflux for 2 h. The brown precipitate was removed by filtration and the filtrate extracted with chloroform. The extract was washed, dried over Na_2SO_4, and evaporated to give a light yellow oil (180 mg). Preparative t.l.c. gave the diol (11) (70 mg), $C_{15}H_{26}O_3$, M^+ 254; $[\alpha]_D$ −28.4° (*c* 0.62); *m/e* 254, 236, 221, 218, 196, 113, 95, 85, 71, 55, and 43; $\nu_{max.}$ 3 500, 1 723, 1 410, 1 390, 1 380, and 1 360 cm^{-1}; δ 0.40 (2 H, m), 1.05, 1.17, 1.23 and 2.13 (each 3 H, s), and 2.36 (2 H, t, *J* 7.0 Hz).

Oxidation of the Keto-diol (11) *with Sodium Metaperiodate*.—To a solution of compound (11) (30 mg) in methanol (1.5 ml) a solution of $NaIO_4$ (45 mg) in water (1.5 ml) was added, and the mixture left at room temperature for 3 days. Water was added to the mixture, which was then extracted with ether. The extract was washed, dried (Na_2SO_4), and evaporated to afford a light yellow oil (30 mg). Preparative t.l.c. gave the triketone (12) (23 mg) (Found: M^+, 252.173 1. $C_{15}H_{24}O_3$ requires *M*, 252.172 4); $[\alpha]_D$ −50.2° (*c* 0.53); *m/e* 252, 237, 194, 179, 136, 113, 95, 85, 55, and 43; $\nu_{max.}$ 1 725, 1 695, 1 450, 1 420, 1 390, 1 385, 1 365, and 1 165 cm^{-1}; δ 1.16 (6 H, s) and 2.08 (6 H, s); $\lambda_{max.}$ (iso-octane) 203 nm (ε 3 000).

Ozonolysis of (−)-*Taylorione* (1) *and Methylation of the Acid* (13) *into the Ester* (14).—Ozonized O_2 was passed through a solution of the ketone (1) (110 mg) in ethyl acetate (15 ml) at −15 °C for 3 h. After evaporation of the solvent *in vacuo* the ozonide was decomposed with water containing a few drops of H_2O_2 on a steam-bath for 1 h. The reaction mixture was extracted with ether (× 3) and the extract concentrated. Preparative t.l.c. gave the acid (13) (75 mg), $C_{10}H_{16}O_3$, $[\alpha]_D$ −20.6° (*c* 1.02); *m/e* 149 (M^+ − 35), 131, 101, 85, 69, and 43; $\nu_{max.}$ 3 500—2 500, 1 720, 1 695, 1 413, 1 383, 1 370, 1 363, 1 230, 1 165, 1 125, and 997 cm^{-1}; δ 1.19, 1.25, and 2.08 (each 3 H, s). The acid (70 mg) was then methylated by treatment with an ethereal solution of CH_2N_2. Evaporation of the reaction mixture *in vacuo* followed by preparative t.l.c. gave the methyl ester (14) (60 mg), $C_{11}H_{18}O_3$, $[\alpha]_D$ −25.1° (*c* 0.3) {lit.,[7] $[\alpha]_D$ +27.4° (*c* 1.0, $CHCl_3$)}; *m/e* 198 (M^+). 197, 183, 167, 166, 154, 140, 127, 109, 95, 81, 67, and 43; $\nu_{max.}$ 1 720, 1 375, 1 360, 1 180, 1 130, 1 095, 935, and 840 cm^{-1}; δ 1.16, 1.20, 2.07, and 3.60 (each 3 H, s), 1.45 (1 H, d, *J* 9.0 Hz), 2.28 (2 H, d, *J* 6.0 Hz) [lit.,[7,8] δ ($CHCl_3$) 1.07, 1.2, 2.09, and 3.63 (each 3 H, s), and 2.3 (2 H, d, *J* 6 Hz); δ 1.16, 1.23, 2.13, and 3.62 (each 3 H, s), and 1.44 (1 H, d, *J* 9.4 Hz)].

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