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NEW TETRAHYDROPYRANS FROM A MARINE SPONGE

ROBERT J. CAPON, EMILIO L. GHISALBERTI and PHILLIP R. JEFFERIES
Department of Organic Chemistry, University of Western Australis, Nedlands, 6009, Western Australia

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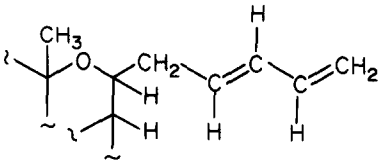
Abstract—Two new tetrahydropyrans have been isolated from the sponge *Haliclona sp.* From chemical and spectroscopic evidence they are shown to be (1'R, 2S, 2"E, 5R, 6R)-2-(1'-bromethyl)-2,5-dimethyl-6-(penta-2",4"-dienyl)-tetrahydropyran and (1'R, 2S, 5R, 6R)-2-(1'-bromoethyl)-2,5-dimethyl-6-(pent-4"-enyl)-tetrahydropyran.

In continuation of our work on the natural products from marine sources of the Western Australian coast, we have examined the metabolites of a *Haliclona sp.* (Order: Haplosclerida; Family: Halicloniidae). The sponge† was collected at a depth of 10 m off Cosy Corner on the South-West Coast of Western Australia. From chemical and spectroscopic evidence the major components isolated have been shown to contain a 2,2,5,6-tetrasubstituted tetrahydropyran ring. The evidence for their structure and absolute configuration is the subject of this report.

Silicic acid and alumina chromatography of the CH_2Cl_2 extract from the sponge afforded a mobile oil (0.6% dry wt) which from glc appeared as a mixture of two components (2 : 1). Pure samples of each were obtained as clear volatile oils by preparative GC.

The major component (**1**) showed M + 1 peaks at *m/z* 287/289 in the CI_{CH_4} mass spectrum suggesting the presence of a Br atom whereas the highest mass ions in the EI mass spectrum appeared at *m/z* 219 and 221 (219.038; $C_9H_{16}{}^{79}BrO$) resulting from a loss of a C_5H_7 fragment from the molecular ion. Thus the molecular formula is $C_{14}H_{23}BrO$. Significant ions at *m/z* 107/109 (C_2H_4Br) were also apparent in the EI-MS of **1**. The presence of a 1-bromoethyl moiety was inferred from the ^{1}H-NMR of **1** which included a quartet at δ4.72 (J 6.9 Hz) and was shown to be coupled only to a secondary Me (δ 1.64, J 6.9 Hz). Other signals in the ^{1}H-NMR spectrum included a singlet (δ 1.27) for a tertiary Me group, a doublet (δ 0.93, J 6.9 Hz) for a secondary Me group, a dt (δ 3.53, J 2.5, 7.0 Hz) assigned to an oxymethine proton and a complex pattern in the vinylic proton region which from NMDR experiments could be assigned to a five-proton spin system of a monosubstituted butadiene moiety [λ_{max}224(ε 13300)]. Furthermore, a dt (J 14.5, 7.0 Hz) at δ 5.63 was shown to have the small coupling from an allylic methylene group at δ 2.16 and the large coupling from a vinylic proton, indicating that the butadiene unit was part of an (2E)-penta-2,4-dienyl system. Irradiation of the methylene group at δ 2.16 also simplified the oxymethine signal from a dt to a d (J 2.5 Hz). Since the IR spectrum of **1** lacked absorption for OH or CO groups the presence of an ether oxygen was inferred. The substitution at the termini for the ether linkage was evident from the ^{13}C-NMR spectrum of **1** which included signals at δ 76.1 (s) 72.6 (d). The first carbon which alone is fully substituted must also bear the tertiary methyl group observed at δ 1.26 in the ^{1}H-NMR spectrum, whereas the second carbon is substituted by an oxymethine proton (δ 3.53) and the (2E)-penta-2,4-dienyl group. These considerations point to partial structure **A** for compound **1**.

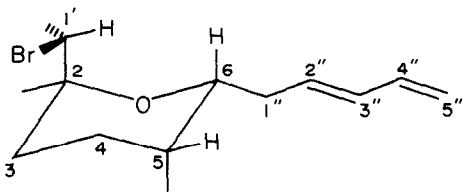


A

The minor component **2**, $C_{14}H_{25}BrO$, contained one less degree of unsaturation. ^{1}H- and ^{13}C-NMR characteristics were also consistent with partial structure A containing only the terminal double bond. In fact, hydrogenation of a mixture of **1** and **2** afforded a single saturated product **3**, $C_{14}H_{27}BrO$. The facile loss of a C_2H_4Br fragment in the MS of **2**, and ready formation of a C_2H_4Br fragment in the MS of **1**, together with the lack of further coupling of the bromomethine proton, suggested that the 1-bromomethyl moiety was located α- to the ether oxygen. This together with the fact that the oxymethine proton appears as a doublet of triplets and the necessity of incorporating a secondary methyl group in the molecule allows extension of partial structure **A** to structure **1** for the major component and **2** for the minor component.

Chemical evidence for the structures proposed was obtained as shown in Scheme 1. Thus, the presence of an α-bromoether moiety was established by Zn–AcOH reduction of **3** to give the unsaturated alcohol (**4**) which could be hydrogenated to the alcohol (**5**). Treatment of **5** with pyridinium dichromate (PDC) gave the ketone **6** which on Baeyer–Villiger oxidation yielded the alkyl hexanoate ester **7**. Hydrolysis of **7** afforded alcohol **8** and an acid (**9**) which was shown to be identical to hexanoic acid. The spectral characteristics of compounds **4–8** were consistent with the structures depicted. The fragmentations observed in the MS of the unsaturated ketone (**10**) obtained by PDC oxidation of **4** provided supporting evidence for the assignment of structure and the origin of the major ions which were mass-matched is given in Scheme 2. Thus, the two compounds from the sponge are shown to be 2 - (1 - bromoethyl) - 2,5 - dimethyl - 6 - (penta - 2,4 - dienyl) - tetrahydropyran (**1**) and 2 - (1 - bromethyl) - 2,5 - dimethyl - 6 - (pent - 4 - enyl) - tetrahydropyran (**2**).

†A specimen has been deposited with the Western Australian Museum (Catalogue No.: WAM-425-81).



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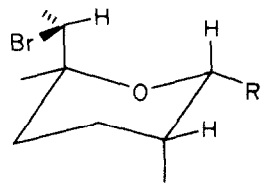
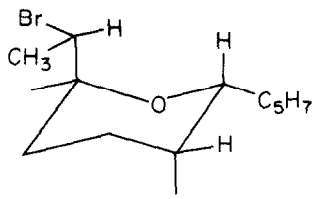


2 R = $CH_2CH_2CH_2CH{=}CH_2$

3 R = $(CH_2)_4CH_3$



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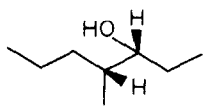

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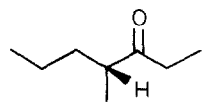

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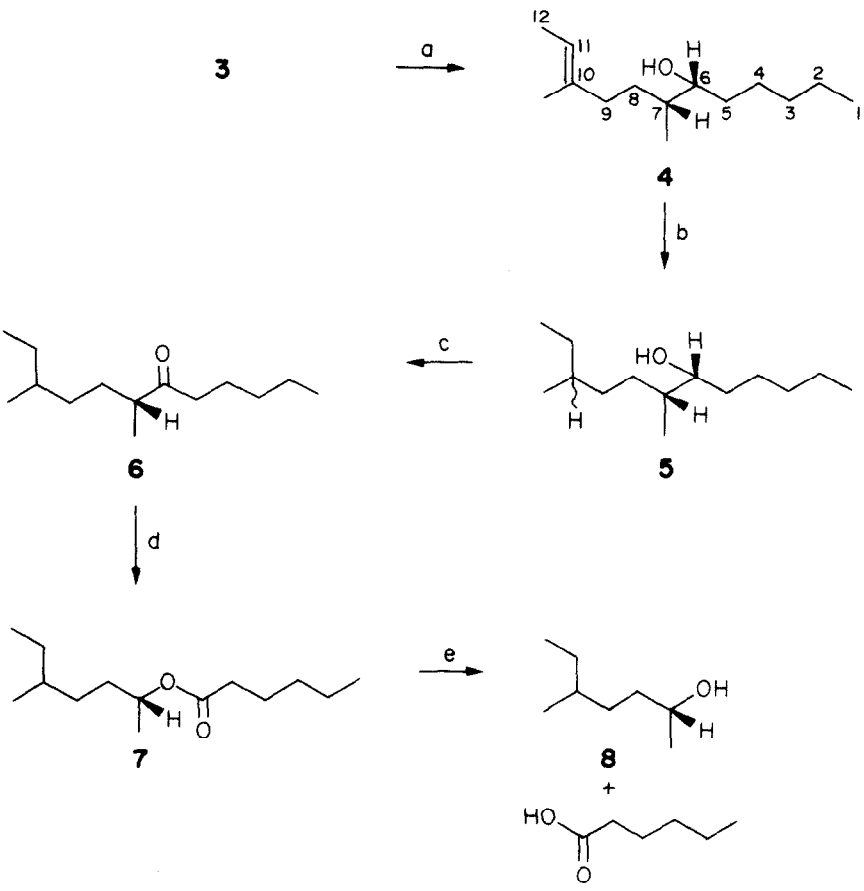
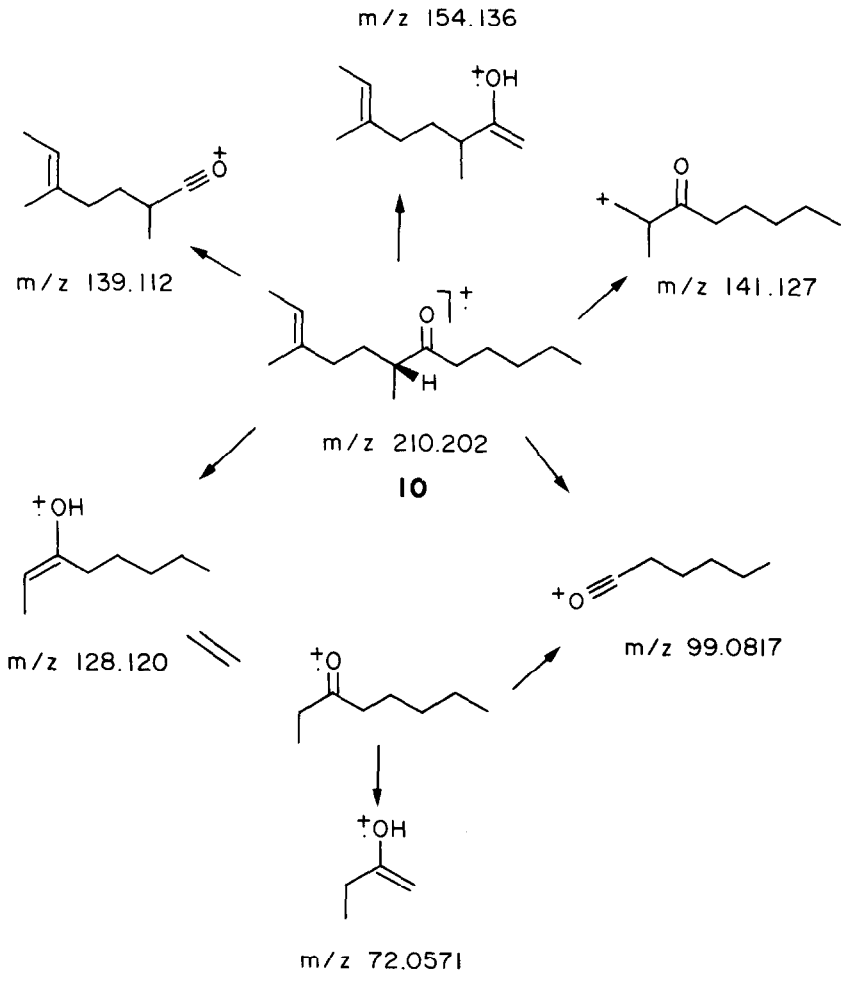


Scheme 1. a, Zn/HOAc; b, H_2, Pd/C; c, PDC; d, *m*-$ClC_6H_4CO_3H$; e, NaOH.



Scheme 2

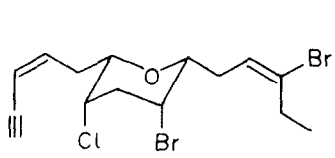
Relative and absolute configuration

Compounds **1** and **2** both contain four chiral centres, three of which are at C2, 5 and 6 on the tetrahydropyran ring and the remaining one relates to the 1-bromoethyl side chain. Consideration of the preferred chair conformations for the tetrahydropyran ring for **1** and **2** suggest that the conformation in which the C6 alkyl side chain adopts the equatorial position is favoured since if it were axial there must be a 1,3-diaxial interaction with one or other substituent at C2. The coupling constant observed in the ^{1}H-NMR spectrum of **1** between the hydrogens at C5 and C6 is small (J 2.5 Hs), indicative of an axial-equatorial interaction, and therefore requiring the C5 methyl group to have an axial orientation.

An NOE (18%) observed between the C6 oxymethine proton and the C1′-bromomethine in **1** establishes the *cis* 1,3-diaxial orientation of the 1-bromoethyl substituent at C2 and the C6 oxymethine proton. These observations allow the relative configuration of the substituents on the tetrahydropyran ring to be assigned as shown in structure **11** (or its enantiomer).

Application of the Horeau method[1] to determine the absolute configuration of the secondary alcohol in **4** indicated the chirality at the carbinol centre as R. This in turn allows the assignment of a 2S,5R,6R-absolute configuration for compounds **1–3**. Supporting evidence for the chirality assigned to C5 and 6 is available from the close agreement between the molecular rotations of the known (3R, 4R)-4-methylheptan-3-ol (**12**) ($[M_D]+30°$)[2] and (4R)-4-methylheptan-3-one (**13**) ($[M_D]-28°$)[2] with those observed for the saturated alcohol (**5**) ($[M_D]+30°$) and ketone (**6**) ($[M_D]-26°$). The basis for this comparison comes from the work of Carman[3] who showed that for a large number of labdane diterpenes in which two asymetric centres are separated by at least two methylene groups, the molecular rotations of the two portions is approximately additive. In the case of **5** and **6**, if, as is likely, they contain equal amounts of diastereoisomers epimeric at C10, the contribution of C10 averages to zero.

Finally, the chirality at the C1′ centre was established by determining the configuration of the olefin in the reductive debromination product (**4**). In the ^{13}C-NMR spectrum of **4** all Me carbons resonate upfield of 20 ppm indicating that C-12 and the C-10 Me carbon are *cis*- to each other and the appearance of C-9 at 32 ppm suggest that this carbon suffers no steric shielding from a *cis*-Me.[4–6] This establishes the E-configuration of the double bond in **4** and since the reductive debromination is known to proceed in a *trans*-manner the stereochemistry at C1′ in **1** and **2** can be assigned as R. These results allow the absolute configuration of **1** and **2** to be assigned



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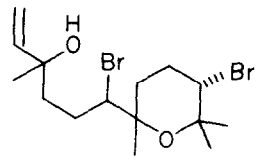

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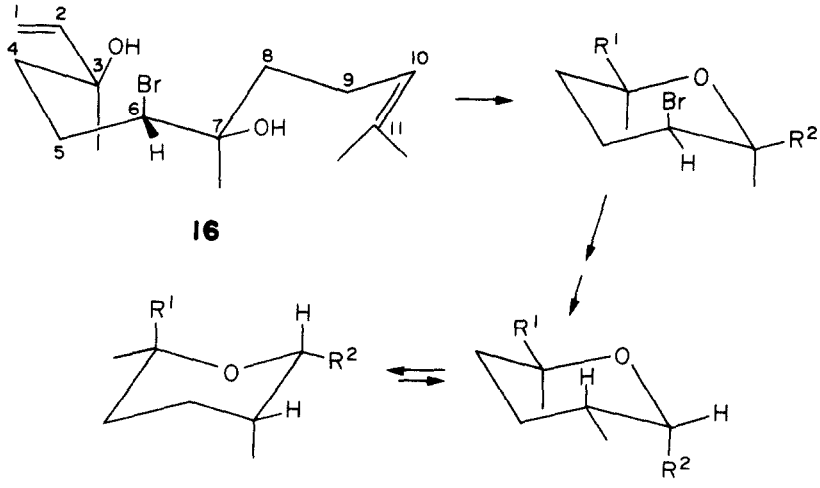

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as (1'R,2S,2''E,5R,6R) - 2 - (1' - bromoethyl) - 2,5 - dimethyl - 6 - (penta - 2'',4'' - dienyl) - tetrahydropyran and (1'R,2S,5R,6R) - 2 - (1' - bromoethyl) - 2,5 - dimethyl - 6 - (pent - 4'' - enyl) - tetrahydropyran, respectively.

A number of cyclic ethers have been isolated from marine sources[7,8] but only two tetrahydropyrans, dactylyne (**14**) from *Aplysia dactylomela*[8] and obtusenol (**15**) from *Laurencia obtusa*,[9] have so far been described. The biosynthetic origin of the metabolites **1** and **2** from *Haliclona* sp. is not obvious. However, a comparison with the structure of obtusenol (**15**) raises the possibility that **1**, **2** and **15** may be derived from a common acyclic sesquiterpene precursor (**16**) which can be considered to arise by addition of Br^+ and H_2O to the internal double bond of nerolidol. Cyclization initiated by Br^+ to the C10-double bond (farnesol numbering) and intervention by the tertiary OH group at C7 leads to the tetrahydropyran system in obtusenol (**15**). On the other hand, displacement of the C7 OH by the C3 OH would generate the brominated tetrahydropyran (**17**) which can then undergo a 1,2-Me shift, addition of hydride ion and conformational inversion to give the tetrahydropyran skeleton of **1** and **2**.

If the reasonable assumption is made that the nerolidol precursor contains a double bond at C6 in the E-configuration then it is necessary to invoke the displacement of the C7 OH by the C3 OH to achieve the stereochemical requirements for the 1,2-Me shift and the absolute stereochemistry shown for the metabolites from *Haliclona* sp. Modification of the R^1 and R^2 groups could presumably occur before or after cyclization.

EXPERIMENTAL

General experimental details have been described.[10]

Extraction of Haliclona sp. A sample of this sponge (172 g, dry wt), collected at a depth of 10 m off Cosy Corner on the South-West Coast of Western Australia, was diced and extracted with CH_2Cl_2 : MeOH (1 : 1). The CH_2Cl_2 layer, obtained after addition of 10% by volume of H_2O, was dried and the solvent was evaporated to give a dark green mobile oil (7.0 g). This extract was rapidly filtered through silicic acid using light petroleum-CH_2Cl_2 (20% gradient) and the non-polar fraction (1.1 g) obtained with light petroleum-CH_2Cl_2 (1 : 1) as a pale yellow oil was adsorbed on a column of Al_2O_3 (neutral, Act. III). Elution with light petroleum-CH_2Cl_2 (1 : 1) gave a clear mobile oil (1.0 g, 0.6% dry wt). Analysis by GC (3% Carbowax 20 M on Chromosorb 85/100, glass column 2 m × 2 mm, isothermal at 170°) revealed the presence of two compounds in a 2 : 1 ratio. Preparative GC (5% Carbowax 20 M on Chromosorb 60/80, glass column 1 m × 5 mm, isothermal at 140°) of a portion (300 mg) of this oil afforded **1** (141 mg) and **2** (80 mg).

(1'R,2S,2''E,5R,6R) - 2 - (1' - *Bromoethyl*) - 2,5 - *dimethyl* - 6 - (*penta* - 2'',4'' - *dienyl*) - *tetrahydropyran* (**1**), a clear volatile oil, b.p. 103° (bath)/0.5 mm, $[\alpha]_D$ 27.3° (*c* 0.3; $CHCl_3$) (Found: 219.039. $C_{19}H_{16}{}^{79}BrO$ requires: 219.038). ν_{max} (film) 3090, 1660, 1610 cm^{-1}; λ_{max} (EtOH) 224 nm (ϵ 13300); ^{1}H-NMR ($CDCl_3$, 80 MHz) δ: 0.93 (d, J 6.6 Hz, 5 Me), 1.27 (s, 2 Me), 1.64 (d, J 6.9 Hz, 1' Me), 3.53 (dt, J 2.5, 7.0 Hz, H6), 4.72 (q, J 6.9 Hz, H1'), 4.9–5.3 (m, $(H5'')_2$), 5.63 (dt, J 14.5, 7.0 Hz, H2''), 5.9–6.6 (m, H3'' and H4''); ^{13}C-NMR ($CDCl_3$, 20.1 MHz)δ: 11.3 (q, C5-CH_3), 19.4 (q, C2'), 23.3 (q, C2-CH_3), 26.5 (t, C4), 27.8 (t, C3), 29.5 (d, C5), 36.8 (t, C1''), 50.0 (d, C1'), 72.6 (d, C6), 76.1 (s, C2), 115.5 (*t*, C5''), 131.4, 133.2 (d, C2'' and C3''), 137.2 (*d*, C4''). MS (Cl_{CH_4}) (*m*/*z*, %): 287/289 (M + 1, 5), 269/271 (3), 219/221 (22), 208 (15), 207 (100), 189 (55), 139 (57), 121 (15); MS (EI): 219/221 (M^+-C_5H_7, 14), 201/203 (3), 139 (40), 121 (67), 111 (18), 107/109 (9), 93/95 (22), 79/81 (25), 67 (100).

(1'R,2S,5R,6R) - 2 - (1' - *Bromoethyl*) - 2,5 - *dimethyl* - 6 - (*pent* - 4'' - *enyl*) - *tetrahydropyran* (**2**), a clear volatile oil, b.p. 82° (bath)/0.5 mm, $[\alpha]_D$ 25.4° (*c*, 0.3; $CHCl_3$) (Found: 181.159. $C_{12}H_{21}O$ requires: 181.159). ν_{max} (film) 3080, 1645 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 80 MHz) δ: 0.90 (d, J 6.9 Hz, 5 Me), 1.26 (s, 2 Me), 1.66 (d, J 6.9 Hz, 1' Me), 3.48 (m, H6), 4.74 (q, J 6.9 Hz, H1'), 4.8–5.2 (m, $(H5'')_2$), 5.82 (ddt, J 17.0, 10.0, 6.5 Hz, H4''); ^{13}C-NMR ($CDCl_3$, 20.1 MHz) δ: 11.4. (q, C5-CH_3), 19.4 (q, C2'), 23.3 (q, C2-CH_3), 25.6 (t, C1''), 26.6 (t, C4), 28.0 (t, C3), 29.9 (d, C5), 33.2, 33.9 (t, C2'' and C3''), 50.1 (d, C1'), 72.4 (d, C6), 75.8 (s, C2), 114.7 (t, C5''), 133.8 (d, C4''). MS (CI_{CH_4}) (*m/z*, %): 289/291 (M + 1), 4), 271/273 (2), 219/221 (2), 210 (17), 209 (100), 191 (60), 139 (10); MS (EI): 181 (M^+–C_2H_4Br, 57), 163. (38), 123 (36), 109 (14), 107 (28), 95 (31), 93 (11), 81 (78), 79 (15), 69 (70), 43 (100).

(1'R,2S,5R,6R) - 2 - (1' - *Bromoethyl* - 2,5 - *dimethyl* - 6 - *pentyltetrahydropyran* (**3**). Hydrogenation of a mixture of **1** and **2** in ether over 10% Pd/C under H_2 at rt afforded **3** as a clear volatile oil, b.p. 100° (bath)/0.5 mm, $[\alpha]_D$ 21° (*c*, 0.1; $CHCl_3$) (Found: C, 57.44; H, 9.29. $C_{14}H_{27}BrO$ requires C, 57.73; H, 9.34%). ^{1}H-NMR ($CDCl_3$, 80 MHz) δ: 0.90 (d, J 6.8 Hz, 5 Me), 1.26 (s, 2 Me), 1.66 (d, J 7.4 Hz, 1 Me), 3.43 (m, H6), 4.74 (q, J 7.4 Hz, H1'); ^{13}C-NMR ($CDCl_3$, 20.1 MHz) δ: 11.4 (q, C5-CH_3), 14.0 (q, C5''), 19.4 (q, C2'), 22.7 (t, C4''), 23.3 (q, C2-CH_3), 25.8 (t, C1''), 26.6 (t, C4), 28.0 (t, C3), 29.9 (d, C5), 32.1 (t, C2''), 33.7 (t, C3''), 50.2 (d, C1'), 72.5 (d, C6), 75.7 (s, C2). MS (EI) (*m/z*, %): 183 (M^+–C_2H_4Br, 42), 165 (5), 123 (3), 71 (30), 69 (64), 43 (100).

(6R,7R,10E) - 7,10 - *Dimethyldodec* - 10 - *en* - 6 - *ol* (**4**). A soln of **3** (123 mg) in AcOH (2 ml) and H_2O (0.15 ml) was treated with activated Zn dust (100 mg) at 45–50° for 1 hr. The soln was filtered and the filtrate was diluted and extracted with ether to yield the *unsaturated alcohol* **4** (70 mg), as a clear oil, b.p. 100° (bath)/1.0 mm, $[\alpha]_D$ 18.5° (*c*, 0.3; $CHCl_3$) (Found: 212.214. $C_{14}H_{28}O$ requires: 212.214). ν_{max} (film) 3400, 1675 cm^{-1}; λ_{max} (EtOH) 202 nm (ϵ 1500). ^{1}H-NMR ($CDCl_3$, 80 MHz) δ: 0.87 (d, 6.0 Hz, 7 Me), 1.60 (s, 11 Me), 1.8–2.1 (bm, $(H9)_2$), 3.53 (bm, H6), 5.22 (bm, H11); ^{13}C-NMR ($CDCl_3$, 20.1 MHz) δ: 13.3 (q, C12), 13.6 (q, C1), 14.1 (q, C7-CH_3), 15.7 (q, C10-CH_3), 22.7 (t, C2), 26.0 (t, C4), 31.8, 32.1 (t, C8 and C9), 34.6 (t, C3), 37.5 (t, C5), 37.9 (t, C7), 75.3 (d, C6), 118.5 (d, C11), 136.2 (s, C10). MS (EI) (*m/z*, %): 212 (M^+, 9), 194 (2), 141 (34), 137 (3), 82 (89), 70 (31), 69 (45), 55 (100), 43 (58).

(7R,10E) - 7,10 - *Dimethyldodec* - 10 - *en* - 6 - *one* (**10**). Treatment of **4** (30 mg) as described below for the conversion of **5** and **6**, afforded the *unsaturated ketone* **10** (25 mg) as an oil, $[\alpha]_D$–17.1° (*c*, 0.7; $CHCl_3$) (Found: M^+, 210.202. $C_{14}H_{26}O$ requires: 210.198). ν_{max} (film) 1715 cm^{-1}; λ_{max} (EtOH) 202 nm (ϵ 6000). ^{1}H-NMR ($CDCl_3$, 80 MHz) δ: 0.5–2.8 (m, 11 H), 0.89 (t, J 7.0 Hz, $(H1)_3$), 1.05 (d, J 6.8 Hz, 7 Me), 1.26 (brs, 10 Me), 1.58 (brs, $(H12)_3$), 2.42 (bt, J 8.0 Hz, $(H9)_2$), 5.19 (m, H11). MS (EI) (*m/z*, %): 210 (M^+, 16), 154.136 (10, $C_{10}H_{18}O$ requires 154.136), 141.127 (9, $C_9H_{17}O$ requires: 141.128), 139.112 (12, $C_9H_{15}O$ requires: 139.112), 128.120 (21, $C_8H_{16}O$ requires: 128.120), 99.0817 (91, $C_6H_{11}O$ requires: 99.081), 72.0571 (100, C_4H_8O requires: 72.058).

Determination of the absolute configuration of **4** *by Horeau's method.*[1] The alcohol **4** (27 mg, 0.13 mmol) was added to a 12.5% soln of (±)-2-phenylbutyric anhydride in anhyd pyridine (0.64 ml, 0.26 mmol of anhydride) and the mixture stirred at rt for 1 hr. The excess anhydride was decomposed with H_2O and the phenylbutyric acid titrated with NaOH (esterfication yield 69%). The basic soln was extracted wtih benzene, acidified and re-extracted with benzene to give 2-phenylbutyric acid, $[\alpha]_D$ 1.7° (*c*, 0.6; $CHCl_3$), optical yield 7.2%. Prolonged esterification of a second sample of **4** (14 mg) over 24 hr yielded 2-phenylbutyric acid, $[\alpha]_D$ 7.9° (*c*, 1.3; $CHCl_3$) optical yield 25%.

(6R,7R,10ξ)-7,10-*Dimethyldodecan-6-ol* (**5**). Hydrogenation of a soln of **4** (70 mg) in ether over 10% Pd/C under H_2 afforded the *saturated alcohol* **5** (65 mg) as an oil, $[\alpha]_D$ 14° (*c*, 0.3; $CHCl_3$) (Found: M^+–H_2O, 196.215. $C_{14}H_{28}$ requires: 196.219). ^{1}H-NMR ($CDCl_3$, 60 MHz) δ: 3.44 (bm, H6). MS (EI) (*m/z*, %): 196 (M^+–H_2O, 0.5), 143.142 (b, $C_9H_{19}O$ requires: 143.144), 112 (7), 101 (36), 100 (16), 83 (100), 69 (22).

(7R,10ξ)-7,10-*Dimethyldodecan-6-one* (**6**). A soln of **5** (45 mg) in CH_2Cl_2 (2 ml) was treated with pyridinium dichromate (90 mg) at rt for 6 hr. The soln was filtered through Celite and the solvent evaporated to yield the *ketone* **6** as an oil, $[\alpha]_D$–12° (*c*, 0.4; $CHCl_3$) (Found: 212.217. $C_{14}H_{28}O$ requires: 212.214). ^{1}H-NMR ($CDCl_3$, 60 MHz) δ: 0.4–2.7 (bm, 26H), 2.40 (bt, J 6.0 Hz, $(H5)_2$). MS (EI) (*m/z*, %): 212 (M^+, 3), 141 (8), 128 (36), 123 (9), 113 (3), 99 (100), 72 (45), 71 (68), 57 (26), 43 (26).

Degradation of **6** *to hexanoic acid.* A soln of **6** (35 mg) in dry $CHCl_3$ (2 ml) was treated with *m*-chlorperbenzoic acid (42 mg) and *p*-TsOH (1 mg) and stirred for 48 hr at rt after which additional peracid (40 mg) was added. After 92 hr the mixture was diluted with H_2O (20 ml) and extracted with CH_2Cl_2. Recovery of the product afforded the ester **7** (34 mg) as an oil, $[\alpha]_D$ 0° (*c*, 0.3; $CHCl_3$). ν_{max} (film) 1740 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 60 MHz) δ: 0.3–2.5 (bm, 25H), 2.23 (bt, J 6.0 Hz, $(H5)_2$), 4.85 (bm, H2'). MS (EI) (*m/z*, %): 171 (M^+–C_4H_9, 2), 143 (8), 117 (20), 112.124 (24, C_8H_{16} requires: 112.125), 99 (100), 84 (11), 83 (21), 71 (52), 70 (63), 57 (33), 43 (24).

A soln of the ester **7** (30 mg) in H_2O: MeOH (4 : 1) (5 ml) was treated with 2 N NaOH and heated under reflux for 18 hr. Recovery of the neutral component afforded the alcohol **8** which appeared homogenous on GLC analysis, R_t 2.0 min (Carbowax 20M capillary column, 0.3 mm × 25 m, initial temp 90° programmed at 5°/min). MS (EI) (*m/z*, %): 115 (M^+–CH_3, 5), 112 (2), 97 (21), 85 (12), 84 (22), 71 (10), 70 (43), 57 (28), 45 (100). The acidic fraction on extraction with ether afforded a component which was shown to have identical GC and MS characteristics with those of (**9**). GC: R_t 6.0 min (3% Carbowax 20M on Chromosorb 85/100, glass column 2 m × 2 mm, initial temp 110° programmed at 6°/min); MS (EI) (*m/z*, %): 87 (M^+–C_2H_5, 15), 73 (51), 60 (100).

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REFERENCES

[1]A. Horeau, *Determination of the configuration of secondary alcohols by partial resolution* in *Stereochemistry, Fundamentals and Methods* (Edited by H. B. Kagan), Vol. 3, p. 51. Georg Thieme, Stuttgart (1977).
[2]J. P. Vigneron, R. Meric and M. Dhaenens, *Tetrahedron Letters* 2057 (1980).
[3]R. M. Carman, *Aust. J. Chem.* **19**, 629 (1966).
[4]D. E. Dozman, M. Jautelat and J. D. Roberts, *J. Org. Chem.* **36**, 2757 (1971).
[5]H. Brouwer and J. B. Stothers, *Can. J. Chem.* **50**, 1361 (1972).
[6]P. Crews and E. Kho-Wiseman, *J. Org. Chem.* **42**, 2812 (1977).
[7]B. M. Howard, W. Fenical, K. Hirotsu, B. Solheim and J. Clardy, *Tetrahedron* **36**, 171 (1980) and Refs. therein.
[8]F. J. McDonald, D. C. Campbell, D. J. Vanderah, F. J. Schmitz, D. M. Washecheck, J. E. Burks and D. van der Helm, *J. Org. Chem.* **40**, 665 (1975) and Refs. therein.
[9]S. Imre, S. Islimyeli, A. Öztunc and R. H. Thomson, *Phytochemistry* **20**, 833 (1981).
[10]E. L. Ghisalberti, P. R. Jefferies and A. D. Stuart, *Aust. J. Chem.* **32**, 1627 (1979).