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GYMNOMITRANE SESQUITERPENOIDS FROM THE LIVERWORT *MARSUPELLA EMARGINATA* VAR. *PATENS*

AKIHIKO MATSUO,* HIROSHI NOZAKI,† KOJI YANO,‡ SEIRYU UTO,‡ MITSURU NAKAYAMA§ and SIEGFRIED HUNECK‖

Division of Bioscience and Biotechnology, The College of Kure, 2-10-3 Agaminami, Kure-city, Hiroshima 737, Japan; †Department of Biochemistry, Okayama University of Science, Ridai-cho, Okayama 700, Japan, ‡Department of Chemistry, Hiroshima University, Naka-ku, Hiroshima 730, Japan, §Department of Agricultural Chemistry, College of Agriculture, University of Osaka Prefecture, Sakai, Osaka 591, Japan, ‖Institute of Plant Biochemistry, Research Centre for Molecular Biology and Medicine of the Academy of Science of the G D R, GDR-401 Halle, Weinberg, G.D.R

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Key Word Index—*Marsupella emarginata* var *patens*, Hepaticae, bryophyte; gymnomitrane sesquiterpenoids, structural determination; chemosystematic, ring expansion reaction

Abstract—Three new gymnomitrane sesquiterpenoids have been isolated from the liverwort *Marsupella emarginata* var *patens* together with the known (−)-gymnomitrene and (−)-*ar*-curcumene. Their structures and absolute configurations have been determined on the basis of chemical and spectroscopic evidence as well as from the results of an X-ray analysis of a derivative We also describe the ring expansion reaction of the gymnomitrane framework and the chemosystematics of the genus *Marsupella*.

INTRODUCTION

The liverworts often produce unique sesquiterpenoids with novel carbon skeletons which are not isolated from higher plants; most of the liverwort sesquiterpenoids correspond to the enantiomer of those of higher plants [1, 2]. In the course of our investigation on the terpenoid constituents of the genus *Marsupella* (Jungermanniales) [3, 4], we have isolated three new gymnomitrane sesquiterpenoids (**1**–**3**) along with the parent hydrocarbon (−)-gymnomitrene (**4**) and the enantiomeric (−)-*ar*-curcumene (**5**) from *Marsupella emarginata* (Ehrch.) Dum. var. *patens* N. Kitag. The hydrocarbon **4** (syn. pompene and barbatene) framework [5–7] might be biosynthesized by a cyclization reaction of the bicyclic sesquiterpene (+)-bazzanene which is produced through double 1,2-methyl migrations of the cuparane skeleton [8] The structure including the absolute configuration of the major alcohol was verified to be (−)-gymnomitr-3(12)-en-15-ol (**1**) by single crystal X-ray analysis of the *p*-bromobenzoate (**8**) of the nor-ketone derivative (**7**). The structures of two other compounds, the sesquiterpene aldehyde **2** and the sesquiterpene acid **3**, were determined by chemical correlation with the alcohol (**1**) as (−)-gymnomitr-3(12)-en-15-al (**2**) and (−)-gymnomitr-3(12)-en-15-oic acid (**3**).

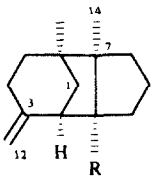
The sesquiterpene hydrocarbon **4** is the most widely occurring in the liverworts. However, a few oxygenated derivatives of the hydrocarbon have been obtained as natural products [9, 10]. Treatment of the tosylate derivative (**9**) of gymnomitrene alcohol (**1**) with lithium aluminium hydride in ether afforded two new sesquiterpene hydrocarbons (**10** and **11**) formed by ring expansion reactions

*Author to whom correspondence should be addressed.

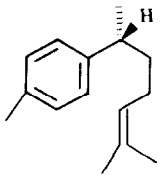
RESULTS AND DISCUSSION

The liverwort, *Marsupella emarginata* var. *patens*, was digested with methanol and the extract partitioned with ethyl acetate. The ethyl acetate extract (2.0% yield) was submitted to a combination of column and thin layer chromatography over silica gel to give three new gymnomitrane sesquiterpenoids (**1**–**3**) in yields of 5.5, 1.8 and 7.7%, respectively, of the ethyl acetate extract The two enantiomeric sesquiterpenes **4** [5] and (−)-*ar*-curcumene (**5**) [11] were also isolated as minor constituents

The first compound, (−)-gymnomitr-3(12)-en-15-ol (**1**), $C_{15}H_{24}O$, mp 88–90°, $[\alpha]_D$ −28.1°, was a tricyclic sesquiterpene alcohol containing a hydroxy methylene [ν_{max} 3620, 3450, 1030 cm^{-1}; δ3.42 (2H, *s*)] as well as an exocyclic methylene [ν_{max} 3065, 1640, 890 cm^{-1}, δ4.59 (2H, *br s*)] and two tertiary methyls [δ0.84 and 0.91 (each 3H, *s*)]. Two other compounds, (−)-gymnomitr-3(12)-en-15-al (**2**), $C_{15}H_{22}O$, $[\alpha]_D$ −10.0°, and (−)-gymnomitr-3(12)-en-15-oic acid (**3**), $C_{15}H_{22}O_2$, mp 131–132°, $[\alpha]_D$ −0.7°, were revealed to be an aldehyde [ν_{max} 1708 cm^{-1}, δ9.51 (1H, s)] and an acid [ν_{max} 3400–2500, 1680 cm^{-1}] respectively, giving a 2,4-dinitrophenylhydroazone, $C_{21}H_{26}O_4N_4$, mp 180–181°, and a methyl ester, $C_{16}H_{24}O_3$, mp 36–37°, respectively The spectroscopic properties suggested they were also tricyclic sesquiterpenoids having two tertiary methyls and an exocyclic methylene. The mass spectral patterns of these compounds (**1**–**3**) exhibiting two significant peaks at *m/z* 93 (or 96) and *m/z* 108 (or 109) as characteristic ions were very close to that of the sesquiterpene hydrocarbon **4** [5, 7] which occurs widely in liverworts. Furthermore, the three sesquiterpenoids **1**–**3** were correlated to each other as follows: the alcohol **1** was produced from aldehyde **2** by lithium aluminium hydride reduction, and the methyl



1 R = CH_2OH
2 R = CHO
3 R = COOH
4 R = Me
6 R = COOMe
9 R = $CH_2OSO_2C_6H_4Me$



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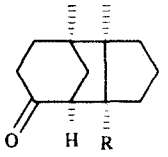
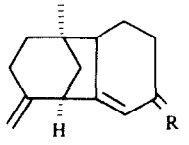
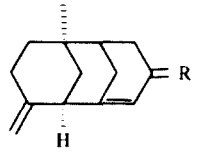


7 R = CH_2OH
8 R = $CH_2OCOC_6H_4Br$



10 R = H_2
12 R = O



11 R = H_2
13 R = O

ester **6** derived from the acid **3** was also transformed into the alcohol **1**.

Because of the limited availability of **1**–**3** for structural correlation with any known sesquiterpenoids, an X-ray crystallographic study was carried out. The alcohol **1** was oxidized by ozonolysis to afford a nor-ketone (**7**), $C_{14}H_{22}O_2$, mp 244° (decompose); $[\alpha]_D - 33.3°$, which was then converted to a *p*-bromobenzoate (**8**), $C_{21}H_{25}O_3Br$, mp 131–132°, $[\alpha]_D + 10.8°$. The *p*-bromobenzoate (**8**) gave suitable crystals for X-ray analysis. The structure of the nor-keto-benzoate (**8**) was determined by a direct method, and the anomalous scattering factor correction for the bromine atom were introduced into the structure-factor calculation to establish the absolute configuration. The molecular structure of the nor-keto-benzoate **8** including the absolute configuration is shown in Fig. 1, and the bond lengths and bond angles agree with the accepted value [12].

The structures of **1**–**3** are shown by the formulae oxygenated at the C-15 position of **4**. These gymnomitrene sesquiterpenoids are the second reported occurrence of oxygenated gymnomitrane compounds [5]. Although the oxygenated gymnomitrane sesquiterpenoids are very rare, the mother hydrocarbon **4** is the most widely distributed sesquiterpenoid in liverworts [9, 10]. It is also interesting in considering the systematical relationship of the genus *Marsupella* that *M. emarginata* var. *patens* contains the gymnomitrane sesquiterpenoids. However, another two species, *M. emarginata* and *M. aquatica*, biosynthesize the longipinane sesquiterpenoids [3, 4].

Otherwise, reduction of the tosylate **9** derived from the alcohol (**1**) was performed with lithium aluminium hydride in diethyl ether to produce the parent hydrocarbon **4**. However, it did not give the **4** but instead afforded two ring expansion products, **10** and **11**, whose spectroscopic data only indicated two tertiary methyls [**10**: δ0.88 and 0.95 (each 3H, *s*), **11**: δ 1.04 and 1.12 (each 3H, *s*)] together with an exocyclic methylene [**10**: δ 4.32 and 4.49 (each 1H, *t*, $J = 2.5$ Hz), **11**: δ 4.52 (2H, *t*, $J = 1.0$ Hz)] and a trisubstituted double bond [**10**: δ 5.26 (1H, *br t*, $J = 3.5$ Hz), **11**: δ 5.26 (1H, *br t*, $J = 3.5$ Hz)]. In order to certify the structures of the two olefins (**10** and **11**) thus obtained, they were oxidized [CrO_3–(pyridine)$_2$] to produce two enones (**12** and **13**). The spectral data of these enones suggested they should be α,β,β-trisubstituted consisting of a six-membered ring [**12**: ν_{max} 1655 cm^{-1}; λ_{max} 246 nm;

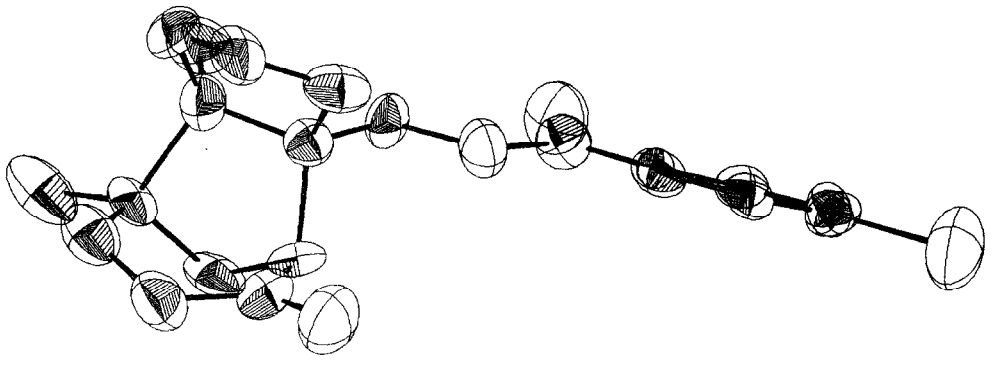


Fig. 1. A perspective view of the *p*-bromobenzoate (**8**).

δ5.77 (1H, *br s*), **13**. ν_{max} 1653 cm^{-1}; ν_{max} 244 nm; δ5.76 (1H, *s*)]. From these data the structures of **11** and **12** consist the 6,5,6-tricyclic and 6,6,6-tricyclic ring systems which can be formed by ring expansion reactions from the gymnomitrane framework (6,5,5-tricyclic ring system)

EXPERIMENTAL

General. Mps. uncorr IR and $[\alpha]_D$. $CHCl_3$ at room temp. ^1H NMR (60 or 90 MHz) and ^{13}C NMR (22 63 MHz). $CDCl_3$ with TMS as int. standard. EIMS 70 eV. UV EtOH CC: Merck kieselgel 60; TLC and prep TLC Merck kieselgel 60 PF_{254}, analytical plates were visualized under UV radiation, I_2 vapour or spraying with 10% H_2SO_4 in EtOH followed by heating at 120°

Plant material and extraction The liverwort, *Marsupella emarginata* var. *patens* was collected in a forest at Futashika in Iwakuni-shi, Yamaguchi-ken The whole plant (410 g) was washed with H_2O, dried in the shade for several days, and extracted 2 × with MeOH for 1 week at room temp The solvent was distilled off under red. pres and oily material obtained was then extracted with EtOAc Removal of the solvent under red pres. gave a viscous oil (8 3 g).

Isolation of the constituents **1–5**. EtOAc extract (4.5 g) was firstly subjected to medium pres. chromatography through a column (44 × 500 mm) of silica gel (230–400 mesh), using hexane containing increasing amounts of EtOAc as eluant. The separated fractions were then applied to prep. TLC on silica gel to isolate the following compounds in order to elution (−)-*ar*-curcumene (**5**) (18 mg), (−)-gymnomitrene (**4**) (20 mg), (−)-gymnomitr-3(12)-en-15-al (**2**) (81 mg), (−)-gymnomitr-3(12)-en-15-oic acid (**3**) (347 mg) and (−)-gymnomitr-3(12)-en-15-ol (**1**) (248 mg). The physical constants and spectroscopic properties of these compounds are listed below

(−)-*Gymnomitr-3(12)-en-15-ol* (**1**) $C_{15}H_{24}O$, mp 88–90°, $[\alpha]_D$ −28 1° (*c* 1 4) IR ν_{max} cm^{-1} 3620, 3450, 3065, 1640, 1030, 890. ^1H NMR (60 MHz). δ 0 84 (3H, *s*), 0.91 (3H, *s*). 2.54 (1H, *d*, *J* = 4.2 Hz), 3 42 (2H, *s*), 4 59 (2H, *br s*) MS *m/z* (rel int.) 220 $[M]^+$ (8%), 205 (3), 202 (19), 189 (13), 145 (7), 133 (11), 119 (18), 108 (86), 93 (100), 79 (50), 67 (31), 55 (27), 41 (36).

(−)-*Gymnomitr-3(12)-en-15-al* (**2**). $C_{15}H_{22}O$, oil, $[\alpha]_D$ −10 0° (*c* 0.5), IR ν_{max} cm^{-1} 1708, 1680, 1085, 890 ^1H NMR (60 MHz): δ 0.90 (3H, *s*), 0.99 (3H, *s*), 2.74 (1H, *d*, *J* = 4 3 Hz), 4 66 (2H, *br s*), 9.51 (1H, *s*) MS *m/z* (rel int): 218 $[M]^+$ (4), 203 (5), 200 (4), 189 (9), 147 (8), 133 (11), 119 (12), 108 (100), 93 (84), 79 (48), 66 (27), 55 (36), 41 (58). 2,4-Dinitrophenylhydrazone mp 180–181°, $[\alpha]_D$ + 123° (*c* 1 0), $C_{21}H_{28}O_4N_4$ (Found C, 62.94, H, 6 81; N, 14 13, requires C, 62.98, H, 7 05, N, 13 99%).

(−)-*Gymnomitr-3(12)-en-15-oic acid* (**3**). $C_{15}H_{22}O_2$, mp 131–132°; $[\alpha]_D$ −0.7° (*c* 1 4), IR ν_{max} cm^{-1} 3400–2500, 3060, 1680, 1640, 1265, 1090, 890 ^1H NMR (60 MHz) δ 0 91 (3H, *s*), 1.12 (3H, *s*), 2 95 (1H, *d*, *J* = 4.8 Hz), 4 66 (2H, *br s*) ^{13}C NMR (22.63 MHz). δ 24.6 (*q*), 24 6 (*q*), 28 2 (*t*), 30.4 (*t*), 33 0 (*t*), 34 8 (*t*), 37.9 (*t*), 42 9 (*s*), 49 3 (*t*), 50.5 (*d*), 59 8 (*s*), 67 8 (*s*), 109.7 (*t*), 149 7 (*s*), 184.9 (*s*). MS *m/z* (rel int): 234 $[M]^+$ (3), 189 (2), 127 (24), 109 (100), 93 (48), 79 (24), 67 (10), 55 (10), 39 (9).

(−)-*Gymnomitrene* (**4**) $C_{15}H_{24}$, oil, $[\alpha]_D$ −16 9° (*c* 0.6), IR ν_{max} cm^{-1}: 3060, 1635, 1385, 1372, 892 ^1H NMR (60 MHz): δ 0.82 (3H, *s*), 0 89 (3H, *s*), 1 03 (3H, *s*), 4.53 (2H, *br s*) MS *m/z* (rel. int.): 204 $[M]^+$ (16), 189 (13), 175 (5), 161 (18), 147 (6), 133 (12), 119 (14), 108 (90), 96 (100), 93 (83), 81 (62), 69 (39), 55 (37), 41 (42).

(−)-ar-*Curcumene* (**5**) $C_{15}H_{22}$, oil, $[\alpha]_D$ −30 0° (*c* 0 5), IR ν_{max} cm^{-1} 1512, 1110, 1018, 820. ^1H NMR (60 MHz) δ 1 19 (3H, *d*, *J* = 7 0 Hz), 1.53 (3H, *br s*), 1 65 (3H, *br s*), 2 28 (3H, *s*), 5 11 (1H, *br*), 7.02 (4H, *s*). MS *m/z* (rel int) 202 $[M]^+$ (43), 187 (3), 159 (6), 145 (29), 131 (87), 119 (100), 105 (47), 91 (24), 83 (18), 77 (15), 69 (20), 55 (27), 41 (43)

Lithium aluminium hydride reduction of the aldehyde (**2**) The aldehyde, (−)-gymnomitr-3(12)-en-15-al (**2**) (31 mg) in dry Et_2O (2 ml) was added dropwise to a soln of $LiAlH_4$ (7 mg) in dry Et_2O (3 ml), and the mixture stirred at 0° for 30 min and then at room temp for 30 min The excess hydride was decomposed by addition of ice-H_2O (0 1 ml) and 10% NaOH (0 1 ml) and the ppt. formed filtered off. Work-up gave (−)-gymnomitr-3(12)-en-15-ol (**1**) as crystals (25 mg): mp 88–89°, $[\alpha]_D$ −26.3° (*c* 1 6), its physical and spectral data were identical with those of the natural alcohol **1**

Methylation of the acid **3** *with diazomethane.* An ethereal soln of CH_2N_2 was added to the acid (**3**) (105 mg) in Et_2O (2 ml) and the mixture kept for 4 hr before being worked-up by the usual way, and the methyl ester (**6**) (95 mg) purified by prep TLC. $C_{16}H_{24}O_2$, mp 36–39°, $[\alpha]_D$ −7 2° (*c* 2 0), IR ν_{max} cm^{-1} 3065, 2940, 2865, 1725, 1642, 1182, 1097, 895; ^1H NMR (60 MHz) δ0.91 (3H, *s*), 1.01 (3H, *s*), 2.95 (1H, *d*, *J* = 5 0 Hz), 3.70 (3H, *s*), 4.70 (2H, *br s*), MS *m/z* (rel. int.): 248 $[M]^+$ (17), 217 (4), 189 (9), 141 (44), 109 (100), 93 (66), 79 (44), 67 (21), 55 (23), 41 (40)

$LiAlH_4$ *reduction of the methyl ester* (**6**). A soln of the ester (**6**) (94 mg) in dry Et_2O (3 ml) was added to a suspension of $LiAlH_4$ (43 mg) in dry Et_2O (3 ml), and the mixture was stirred at 0° for 1 hr. The excess of hydride was decomposed by addition of ice-H_2O (0.1 ml) and 10% aq. NaOH (0.1 ml), and work-up afforded **1** (81 mg). Its spectral data and optical rotation were identical with those of the natural alcohol **1**

Ozonolysis of (−)-*gymnomitrenol* (**1**) To a soln of the alcohol (**1**) (61 mg) in EtOAc (10 ml) ozonized O_2 was passed at −70° for 1 5 hr The solvent was evapd under red pres and residue heated with H_2O (5 ml) and 35% H_2O_2 (0 1 ml) at 50–60° for 2 hr From the reaction mixture the nor-ketoalcohol (**7**) was isolated as crystals (55 mg) mp 244° (decompose); $[\alpha]_D$ −33 3° (*c* 0.6), $C_{14}H_{22}O_2$ (Found. $[M]^+$ 222 1603, requires M, 222 1618), IR ν_{max} cm^{-1}. 3605, 3405, 1692, 1406, 1032, 972, ^1H NMR (60 MHz): δ 1.03 (3H, *s*), 1 03 (3H, *s*), 2.65 (1H, *d*, *J* = 5 0 Hz), 3.48 (2H, *s*), MS *m/z* (rel int): 222 $[M]^+$ (14), 204 (10), 191 (63), 186 (7), 173 (7), 163 (13), 147 (12), 135 (13), 109 (37), 127 (9), 95 (58), 81 (89), 67 (42), 55 (73), 41 (100).

Formation of the p-*bromobenzoate* (**8**) *of the keto-alcohol* (**7**). The alcohol (**7**) (45 mg) was dissolved in pyridine (1 ml) and *p*-BrC_6H_4COCl (50 mg) added After 2 days at room temp, the reaction mixture was worked-up as usual and purified by prep. TLC to yield the *p*-bromobenzoate (**8**) as crystals. (32 mg) Mp 131–132°, $[\alpha]_D$ +10.8° (*c* 0 5), $C_{21}H_{25}O_3Br$ (Found C, 62 35, H, 6 30, requires C, 62 22, H, 6.22%) IR ν_{max} cm^{-1} 1704, 1588, 1482, 1404, 1059, 1005, 842, ^1H NMR δ 1 08 (3H, *s*), 1.12 (3H, *s*), 4 20 (2H, *s*), 7.55 (2H, *d*, *J* = 8 5 Hz), 7 88 (2H, *d*, *J* = 8.5 Hz); MS *m/z* (rel. int) 404 $[M]^+$ (9), 402 $[M]^+$ (11), 388 (7), 386 (7), 308 (9), 279 (7), 272 (17), 262 (34), 257 (14), 229 (9), 221 (6), 213 (6), 204 (55), 191 (67), 185 (64), 173 (30), 161 (17), 149 (64), 114 (2), 94 (94), 81 (61), 69 (75), 55 (94), 41 (100)

Preparation of the tosylate **9** *from the alcohol* **1**. To a stirred soln of the alcohol (**1**) (81 mg) in dry pyridine, TsCl (357 mg) was added and stirred for 24 hr at 4° The mixture was worked-up in the usual way to yield a crude product (126 mg) The tosylate **9** (109 mg) was purified by prep. TLC. $C_{22}H_{30}O_3S$; oil, $[\alpha]_D$ +8.3°, (*c* 2 0). IR ν_{max} cm^{-1}: 3070, 3030, 1640, 1600, 1172, 1095, 947, 930, 843, 808. ^1H NMR (60 MHz) δ 0 72 (3H, *s*), 0.78 (3H, *s*), 2 28 (1H, *d*, *J* = 5 0 Hz), 2 31 (3H, *s*), 3 78 (3H, *s*), 4.48 (2H, *t*, *J* = 1 0 Hz), 7 21 (2H, *d*, *J* = 8.5 Hz), 7 62 (2H, *d*, *J* = 8.5 Hz).

Reduction of the tosylate **9**. Under dry N_2 a soln of the tosylate (**9**) (203 mg) in dry Et_2O (5 ml) was added dropwise to a stirred soln of $LiAlH_4$ (117 mg) in dry Et_2O (5 ml). The reaction mixture was stirred for 3 hr, and the usual work-up of the soln gave a

crude product which was purified by prep. TLC containing 10% $AgNO_3$ to yield the two hydrocarbons (**10**: 27 mg and **11** 9 mg) Compound **10** $C_{15}H_{22}$, oil IR ν_{max} cm^{-1} 2940, 2870, 1675, 1648, 1635, 885, 879 ^1H NMR (90 MHz) δ 0 88 (3H, *s*), 0 95 (3H, *s*), 3 10 (1H, *br d*, J = 6 0 Hz), 4 32 (1H, *t*, J = 2 5 Hz), 4 49 (1H, *t*, J = 2 5 Hz), 5 26 (1H, *br t*, J = 3 5 Hz), ^{13}C NMR (22 63 MHz) δ 18 3 (*t*), 21 1 (*q*), 23 7 (*q*), 24 0 (*t* or *s*), 27 9 (*t*), 28 5 (*t*), 36 7 (*t*), 43 7 (*s*), 43 7 (*t*), 44 1 (*s* or *t*), 48 3 (*d*), 102 0 (*t*), 118 3 (*d*), 151 7 (*s*), 155 2 (*s*) MS *m/z* (rel int) 203 $[M]^+$ (100), 187 (67), 173 (50), 159 (27), 145 (46), 131 (38), 107 (51), 91 (54), 79 (44), 67 (18), 55 (26), 41 (42) Compound **11** $C_{15}H_{22}$, oil IR ν_{max} cm^{-1} 3064, 2950, 1712, 1641, 888 ^1H NMR (90 MHz) δ 1 04 (3H, *s*), 1 12 (3H, *s*), 2 32 (1H, *d*, J = 5 0 Hz), 4 52 (2H, *t*, J = 1 0 Hz), 5 26 (1H, *br t*, J = 3.5 Hz) MS *m/z* (rel int) 202 $[M]^+$ (100), 187 (80), 173 (49), 159 (30), 147 (73), 131 (45), 105 (67), 91 (80), 79 (40), 55 (36), 41 (54)

Collins oxidation of **10** *and* **11** The CrO_3-(pyridene)$_2$ complex was prepared in the usual manner from dry pyridine (10 ml) and dry CrO_3 (0 9 g) To a mechanically stirred soln of **10** (24 mg) in dry CH_2Cl_2 (1 ml) was added the above complex as a slurry in dry CH_2Cl_2 (1 ml) at 0° After 24 hr of stirring at room temp. the CH_2Cl_2 soln was passed through a Florisil column and washed with 5% aq HCl The crude product was subjected to prep TLC and afforded **12** (6 mg) Compound **12** $C_{15}H_{20}O$, gum UV λ_{max} nm 246 (ε 10 300) IR ν_{max} cm^{-1} 2955, 2870, 1655, 892, 875 ^1H NMR (90 MHz) δ 0 95 (3H, *s*), 1 18 (3H, *s*), 3 37 (1H, *d*, J = 6 0 Hz), 4 52 (1H, *br t*, J = 1 0 Hz), 4 68 (1H, *br t*, J = 1 0 Hz) 5.77 (1H, *s*) MS *m/z* (rel int) 216 $[M]^+$ (100), 201 (28), 198 (11), 188 (13), 183 (14), 174 (35), 159 (47), 145 (42), 131 (33), 105 (22), 91 (34), 77 (19), 65 (10), 55 (12), 41 (18)

Using the same technique **11** (14 mg) gave the cyclohexenone **13** (8 mg) Compound **13** $C_{15}H_{20}O$, gum. UV λ_{max} nm 244 (ε 6700) IR ν_{max} cm^{-1} 2950, 2860, 1653, 893, 862 ^1H NMR (90 MHz) δ 1 21 (3H, *s*), 1 26 (3H, *s*), 2 69 (1H, *d*, J = 6 0 Hz), 4 68 (2H, *t*, J = 1 0 Hz), 5 76 (1H, *s*) MS *m/z* (rel int) 216 $[M]^+$ (100), 201 (38), 198 (7), 188 (14), 183 (8), 174 (32), 159 (67), 145 (47), 131 (33), 105 (31), 91 (46), 77 (31), 65 (18), 53 (19) 41 (37)

Crystal structure determination of the p-*bromobenzoate* (**8**) Crystal data $C_{21}H_{25}O_3Br$, orthorhombic, a = 7 551 (2), b = 12 302 (6), c = 20 787 (11) Å, U = 1930 9 Å^3, D_c = 1 39 g cm^{-3}, Z = 4, space group $P2_12_12_1$

The intensity data was collected on a Syntex R3 four-circle diffractometer using monochromated MoK_α radiation (λ = 0 7107 Å) The 1184 reflections were judged to be observed after correction for the Lorentz, polarization, and background effects The structure was solved by a direct method using MULTAN in a Syntex XTL program system The subsequent electron density synthesis revealed the non-hydrogen atom skeleton, and the 25 hydrogen atoms were located using the difference electron density synthesis Refinements by the full-matrix least-squares used the anisotropic thermal temperature factors for non-hydrogen atoms and the isotropic ones (B_{iso} 4 5 Å, fixed parameters) for the hydrogen atoms The anomalous scattering factor correction for the bromine atom were introduced into the structure-factor calculations at the last stage to establish the absolute configuration. For this configuration, the R value was 0 078, whereas for the inverted configuration it was 0 090 Further full-matrix least-squares iterations reduced the R factor to 0 076 for 1184 reflections The anisotropic thermal parameters, and the observed and calculated structure factors have been listed as the deposit

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