Synthesis and Transformations of (±)-*trans*-4aβ(*H*),8aα(*H*)-Octahydro-4α,7β-dimethyl-2*H*-1-benzopyran-2-one

Y. S. Sanghvi and A. S. Rao*

National Chemical Laboratory, Poona 411008, India

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Hydrogenation of 4,7-dimethylcoumarin (**1**) in alkaline medium has been shown to furnish a mixture of (±)-*trans*-4aβ(*H*),8aα(*H*)-octahydro-4α,7β-dimethyl-2*H*-1-benzopyran-2-one (**2**), (±)-*trans*-4aβ(*H*),8aα(*H*)-octahydro-4α,7α-dimethyl-2*H*-1-benzopyran-2-one (**3**) and (±)-*cis*-4aα(*H*),8aα(*H*)-octahydro-4ρ,7α-dimethyl-2*H*-1-benzopyran-2-one (**4**) in 40:25:35:ratio, respectively. The stereochemistry of the major hydrogenation product **2**, has been established by transforming it to *p*-menthane derivatives *e.g.* (±)-2 (*R*)-[2′(*R*)-hydroxy-4′(*R*)-methylcyclohex-(1′*S*)-yl]propan-1-ol (**20**) and (±)-*trans*-3*a*,6β-dimethyl-3aβ(*H*),7aα(*H*)-octahydrobenzofuran (**12**). Starting from a mixture of lactones **2**, **3** and **4**, lactone **3** has been obtained in pure state employing a sequence of reactions.

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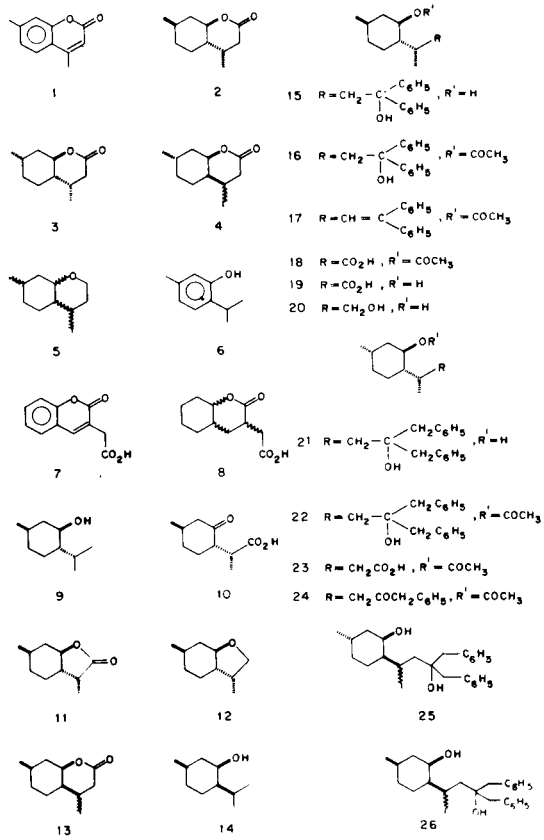
We have been investigating the synthesis of monoterpenes and sesquiterpenes starting from 4,7-dimethylcoumarin (**1**) (1,2). Continuing our studies, we have observed that hydrogenation of 4,7-dimethylcoumarin (**1**) furnished a mixture of lactones **2**, **3** and **4**. Compound **2** has been transformed into a number of compounds related to menthol (**9**). These investigations are presented in this communication.

Hydrogenation of the coumarin **1** was studied by Conner (3), who concluded that the hydrogenation product is a mixture of benzopyrans **5**. We have observed that hydrogenation of the coumarin **7** in alkaline medium furnishes a mixture of octahydrocoumarins **8** (4). Hence it was anticipated that **1** under similar experimental conditions would furnish a mixture of octahydrocoumarins. Hydrogenation of **1** will furnish lactones having four asymmetric centres and this reaction will be of preparative value if a limited number of products are obtained as major components. Literature (5) reports, that *dl*-menthol (**9**) is the major product formed during the hydrogenation of thymol (**6**), suggested that it may be possible to obtain **2** and/or its C_4 epimer as the major components during the hydrogenation of coumarin **1**.

Hydrogenation of **1** was carried out at 180° and 100 kg/cm² (hydrogen pressure) in the presence of aqueous alkali and w-2 Raney-nickel as the catalyst. Acidification of an alkaline solution furnished a mixture of lactones **2**, **3** and **4**. The nmr of the total hydrogenation product exhibited multiplets at δ 3.96 (0.4 H, dt, J = 10 and 4 Hz), δ 4.14 (0.25 H, dt, J = 10 and 4 Hz) and δ 4.54 (0.35 H, narrow multiplet, W ½ = 6 Hz) suggesting that it is a 40:25:35 mixture of the three lactones. The major component exhibiting multiplet at δ 3.96 has been shown to be (±)-**2**. The lactones exhibiting multiplets at δ 4.14 and 4.54 have been tentatively assigned the stereo chemistry **3** and **4** respectively.

The action of phenylmagnesium bromide on the 40:25:35 mixture of lactones (**2**, **3** and **4**) furnished a complex mixture from which diol **15** was isolated as a crystalline solid. Compound **15** was acetylated to give **16**. Acetate **16** was dehydrated by heating in dry benzene in presence of iodine. The resulting elimination product **17** was oxidised with chromium trioxide (6) to furnish the acetoxy acid (±)-**18** as a crystalline compound. Reduction of (±)-**18** with lithium aluminium hydride resulted in the formation of diol (±)**20**, whose nmr spectrum was identical with the nmr spectrum of authentic (−)-**20** (7).

The diol (±)-**20**) obtained from **15** was dehydrated by heating in dry benzene in the presence of *p*-toluenesulfonic acid. The nmr spectrum of the resulting oxide (±)-**12** was identical with the nmr spectrum of an authen-

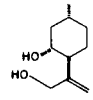


tic sample of oxide (−)-**12** (7). The correlation of the major hydrogenation product **2** prepared from **1** with diol (±)-**20** as well as oxide (±)-**12** conclusively established the stereochemistry of lactone **2** at all the asymmetric centres.

Saponification of acetoxy acid **18** furnished hydroxy acid **19** which was transformed to the *ν*-lactone **11** by heating in dry benzene in the presence of *p*-toluenesulfonic acid. The ir spectrum of the *ν*-lactone thus obtained was superimposable with the ir spectrum of a sample of **11** prepared by Kabaskalian (8) by an alternate route. Oxidation of hydroxy acid **19** gave the keto acid **10**. The nmr spectrum of (±)-2(*R*)[4′(*R*)-methyl-2′-oxocyclohex-(1′*S*)-yl]-propionic acid was comparable with the nmr spectrum of (-)-**10**) prepared by us *via* oxidation of (-)-**20** (7). Foote (9) has reported an alternate synthesis of (-)-**10**.

Lactones **2**, **3** and **4** could not be separated by column chromatography. However, since the diols **21** and **25** derived by the action of benzylmagnesium chloride on a mixture of lactones **2**, **3** and **4** can be separated by fractional crystallization, the transformation of **21** to **3** has been studied since this furnished a convenient method to obtain a pure sample of lactone **3**. Acetylation of diol **21** and subsequent fragmentation (10) with lead tetraacetate-iodine furnished the benzyl ketone **24**. Oxidation of ketone **24** with chromium trioxide furnished the acetoxy acid **23**, which was saponified and the resulting hydroxy acid was cyclised to furnish pure lactone (±)-**3** (free from the stereoisomers **2** and **4**).

Usually the methine proton attached to the lactone oxygen bearing carbon of *trans*-fused octahydrobenzopyran-2-one exhibits a multiplet at δ 3.7 to 3.8 (11,12). The signal exhibited at δ 3.96 (dt, J = 10 and 4 Hz) by the mixture of lactones **2**, **3** and **4** is due to the presence of lactone **2**. The downfield shift of the methine proton is caused by the deshielding effect of the axial methyl group located on the heterocyclic ring. The lactone exhibiting a signal at δ 4.14 (dt, J = 10 and 4 Hz) is assigned the structure **3** since the large downfield shift of the methine hydrogen suggests the presence of two axial methyl groups *syn*-related to the methine proton. The signal patterns (dt; J = 10 and 4 Hz) of methine protons of **2** and **3** clearly show that these protons are axial. The half height width as well as chemical shift of the signal appearing at δ 4.54 in the nmr spectrum of a mixture of lactones **2**, **3** and **4** must be due to a *cis*-octahydrocoumarins (11). Regarding the stereochemistry at C-7, (±)-*cis*-lactone may be **4** or **13**. The compound having stereochemistry **13** should furnish diol **26** which may be expected to show the carbinol *H* signal around δ 4.04 since the carbinol *H* of neoisomenthol (**14**) is reported (13) to show signal at δ 4.04. However, the nmr of the diol (mp 126°) obtained from mixture of lactones **2**, **3** and **4** shows a narrow (m) signal for carbinol *H* at δ 3.61; hence this diol cannot have stereochemistry **26**. Hence the (±)-*cis*-lactone cannot have stereochemistry **13**. The stereochemistry of **4** thus suggested for the (±)-*cis*-lactone appears to be supported by the nmr of the diol **25** (mp 126°), derived from it. The diol mp 126° shows a narrow signal (W ½ = 7 Hz) for the carbinol *H*, suggesting that the carbinol *H* in the diol is equatorial; stereochemistry **25** for the diol mp 126° fits with the data better that the stereochemistry **26**.



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To summarise, **2** has been obtained as the major product through hydrogenation of **1**;**2** has been shown to be an important intermediate for the preparation of a number of compounds (related to menthol) having four asymmetric centres. Lactones **2** may also proved useful for the synthesis of bisabolanes (14,15) of well defined stereochemistry. We have obtained lactone **3** in pure state from a mixture of stereoisomers, through a sequence of reactions and this method may prove useful in the purification of other lactones also.

EXPERIMENTAL

General.

All melting points and boiling points are uncorrected. Infrared spectra were obtained in Nujol or as liguid film on Perkin-Elmer Infracord spectrometer-model 137B or 599B. The nmr spectum of mixture of δ lactones (**2**, **3** and **4**) was recorded on 400 MHz Bruker; other nmr spectra were taken on a Varian T-60 or Bruker WH-90 FT spectrometer using tetramethylsilane as internal standard. Elemental analyses were performed in the microanalytical division of this laboratory.

Hydrogenation of 4,7-Dimethylcoumarin (**1**).

In a 1-litre high pressure rocking type autoclave (18) 4,7-dimethylcoumarin (**1**) (23 g, 0.13 mole), sodium hydroxide pellets (21 g, 0.52 mole), distilled water (200 ml) amd Raney nickel (W-2 6 ml) were charged and heated to 180-190° at 100 kg/cm² (hydrogen pressure) for a period of 8 hours. The reaction mixture was filtered cold and autoclave washed with distilled water (100 ml). The filtrate and washings were acidified with 2*N* hydrochloric acid. Aqueous layer was extracted with solvent ether (3 × 50 ml), washed with water till washings were neutral and dried over sodium sulfate. Evaporation of the solvent left 20.04 g of a thick residue which was distilled under vacuum at 105-110°/0.9 mm to give a 40:25:35 mixture of **2**, **3** and **4**, respectively (18 g, 75%); ir (neat): 1740 (-O-C=O) cm^{-1}; nmr (deuteriochloroform): δ 3.96 (0.4 H, dt J = 10 and 4 Hz), 4.14 (0.25 H, dt, J = 10 and 4 Hz) and 4.54 (0.35 H, narrow multiplet, W ½ = 6 Hz).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.28; H, 9.88.

(±)-1,1-Dipheny-3(*S*)-[2′(*R*)-hydroxy-4′(*R*)-methyl-cyclohex-(1′*S*)-yl]butan-1-ol (**15**).

Phenylmagnesium bromide (0.15 mole) was prepared by treating magnesium pieces (3.6 g, 0.11 mole) in dry ether (100 ml), with bromobenzene (24 g, 0.14 mole). To this soltuion a 40:25:35 mixture of lactones **2**, **3** and **4** (total distillation product obtained after hydrogenation of **1**) (9.1 g; 0.05 mole) in dry ether (50 ml) was added dropwise with cooling at 0° to -5°. The reaction mixture was stirred at 0° for 30 minutes and then

at room temperature for 1 hour, later refluxed for 3 hours and finally decomposed by pouring into cold saturated ammonium chloride solution. The ether layer was separated from the mixture, and the aqueous layer extracted with ether (3 × 50 ml). The combined ether extracts were washed with brine solution, dried over sodium sulfate and the solvent distilled to furnish a viscous residue (14 g). The residue was purified by column chromatography over neutral alumina (grade II, 500 g). Elution was done successively with petroleum ether, petroleum ether/benzene mixture (80:20; 60:40; 40:60; 20:80), benzene, benzene/ethyl acetate (80:20; 60:40; 40:60; 20:80) and methanol. All benzene/ethyl acetate (80:20) fractions were combined and on removal of the solvent furnished 5.3 g (30%) of **15**, mp 120-121°; ir (nujol): 3600, 3400, 2935, 1495, 1450, 1375, 1255, 1190, 1090, 1060, 1050, 1039, 1021, 982, 768, 752, 718 and 700 cm^{-1}; nmr (deuteriochloroform): δ 0.68 (3H, d, J = 6 Hz, -C*H*$_3$), 0.87 (3H, d, J = 6 Hz, -C*H*$_3$), 3.30 (1H, m, *H*C-OH), 7.33 (10H, m, Ar*H*).

Anal. Calcd. for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.73; H, 8.95.

(±)-1,1-Diphenyl-3(*S*)-[2′(*R*)-acetoxy-4′(*R*)-methylcyclohex-(1′*S*)-yl]butan-1-ol (**16**).

A mixture of the diol **15** (5 g, 0.014 mole), pyridine (30 ml) and acetic anhydride (7.14 g, 0.07 mole) was allowed to stand at room temperature for 48 hours. It was diluted with ice water and extracted with solvent ether (3 × 50 ml). The ether extract was washed with 20% aqueous copper sulfate solution, brine water and dried over anhydrous sodium sulfate. Removal of the solvent furnished 5.24 g (95%) of **16**; ir (neat): 3695, 3200, 3100, 2959, 1730, 1600, 1490, 1440, 1365, 1245, 1160, 1130, 1080, 1045, 1020, 966, 898, 769, 736, 720, 709 and 694 cm^{-1}; nmr (carbon tetrachloride): δ 0.68 (3H, d, J = 6 Hz, C*H*$_3$), 0.88 (3H, d, J = 6Hz, C*H*$_3$), 1.66 (3H, s, -OCOC*H*$_3$), 2.43 (1H, s, OH, exchanges with deuterium oxide), 4.52 (1H, broad m, *H*C-OCOCH$_3$), 7.25 (10H, m, Ar-*H*).

Anal. Calcd. for $C_{25}H_{32}O_3$: C, 78.91; H, 8.48. Found: C, 78.68; H, 8.58.

(±)-1,1-Diphenyl-3(*S*)-[2′(*R*)-acetoxy-4′(*R*)-methylcyclohex-(1′*S*)-yl]-but-1-ene (**17**).

A solution of acetoxy alcohol **16** (5 g, 0.13 mole) in dry benzene (50 ml) was refluxed with a crystal of iodine for 12 hours. Dehydration was monitored through tlc and was found to be complete after 20 hours of reflux. The benzene solution was washed with 5% aqueous sodium thiosulfate solution and dried over anhydrous sodium sulfate. Removal of the solvent furnished 4.65 g (97%) of **17**; ir (nujol): 3200, 3100, 2995, 1740, 1600, 1495, 1445, 1360, 1290, 1165, 1140, 1065, 1020, 968, 898, 830, 768, 757, 722 and 695 cm^{-1}; nmr (carbon tetrachloride): δ 0.94 (6H, d, J = 6 Hz, C*H*$_3$) 1.7 (3H, s, OCOC*H*$_3$), 2.5 (1H, broad m, *H*C(CH$_3$)-C=C), 4.66 (1H, dt, J = 10 and 4 Hz, *H*C-OCOCH$_3$), 6.06 (1H, d, J = 10 Hz, *H*C = C), 7.26 (10H, m, Ar-*H*).

Anal. Calcd. for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 83.20; H, 8.49.

(±)-2 (*R*)-[2′(*R*)-acetoxy-4′(*R*)-methylcyclohex-(1′*S*)-yl]propionic Acid (**18**).

A solution of chromium trioxide (2.4 g, 0.024 mole) in water (4 ml) was added during 30 minutes to a vigorously stirred solution of alkene **17** (2.34 g, 0.006 mole) in acetic acid (25 ml). After stirring at room temperature for 16 hours the reaction mixture was worked up in the following manner. Acetic acid was removed under reduced pressure and the residue treated with *N*-hydrochloric acid (50 ml), followed by extraction with ether (3 × 50 ml). The acid **18** was obtained by extracting the ether layer with aqueous sodium bicarbonate (20% solution; 3 × 25 ml) followed by acidification and extraction with ether (3 × 50 ml). The ether extract was dried over anhydrous sodium sulfate and solvent distilled under reduced pressure. The residue was crystallized from petroleum ether to yield 0.90 g (60%) of **18**, mp 121°; ir (nujol): 3000, 2700, 1740, 1700, 1450, 1385, 1340, 1295, 1235, 1135, 1100, 1039, 980, 950, 900 and 845 cm^{-1}; nmr (carbon tetrachloride): δ 0.92 (3H, d, J = 6 Hz, C*H*$_3$), 2.66 (1H, braod m, *H*C-CO$_2$H), 4.51 (1H, dt, J = 10 and 4 Hz, *H*C-OCOCH$_3$), 11.27 (1H, m, CO$_2$*H*).

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 62.97; H, 8.89.

(±)-2(*R*)[2′(*R*)-Hydroxy-4′(*R*)-methylcyclohex-(1′*S*)-yl]propan-1-ol (**20**).

Acetoxy acid **18** (0.22 g, 0.001 mole) in dry ether (25 ml was added with stirring to a suspension of lithium aluminium hydride (0.12 g, 0.003 mole) in dry ether (25 ml) at 0°. Subsequently dry benzene (25 ml) was added and the reaction mixture refluxed for 24 hours. The complex was decomposed (5% aqueous alcohol) and the organic layer separated. The aqueous layer was extracted with ether (2 × 25 ml), the combined ether extracts were washed with water, dried over anhydrous sodium sulfate and the solvent distilled under reduced pressure. The residue was crystallized from petroleum ether to yield 0.15 g (90%) of **20**, mp 74°; nmr (carbon tetrachloride): δ 0.86 (3H, d, J = 7 Hz, C*H*$_3$ on C-4′), 0.92 (3H, d, J = 6 Hz, C*H*$_3$ on C-1), 3.4 (1H, m, *H*C-OH), 3.54 (2H, d, J = 7 Hz, C*H*$_2$OH).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.93; H, 11.59.

(±)-*Trans*-3α,6β-dimethyl-3aβ(*H*),7α(*H*)-octahydrobenzofuran (**12**).

A solution of diol **20** (0.086 g, 0.05 mole) in dry benzene (25 ml) was refluxed with *p*-toluenesulfonic acid (0.020 g). The reaction was monitored through tlc and found to be complete after 12 hours reflux. The benzene solution was washed with aqueous sodium bicarbonate (5%; 25 ml), dried over anhydrous sodium sulfate and solvent removed under reduced pressure to furnish 0.072 g (93%) of **12**; nmr (carbon tetrachloride): δ 0.96 (3H, d, J = 7 Hz, C*H*$_3$ on C-6), 1.00 (3H, d, J = 6 Hz, C*H*$_3$), 3.07 (1H, broad m, *H*C-O-), 3.26 (1H, t, J = 8 Hz, -O-C*H*$_2$), 3.90 (1H, t, J = 8 Hz, -O-C*H*$_2$).

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.51; H, 11.78.

(±)-2(*R*)-[2′(*R*)-hydroxy-4′(*R*)-methylcyclohex-(1′*S*)-yl)]propanoic Acid (**19**).

The acetoxy acid **18** (0.22 g, 1 mmole) was heated under reflux with sodium hydroxide (0.08 g, 2 mmoles) and ethanol (20 ml) for 6 hours. On the usual work up it furnished 0.21 g of residue; it was crystallised from petroleum ether/acetone to yield 0.17 g (95%) of **19**, mp 135°; ir (nujol): 3350, 2995, 2625, 1697, 1445, 1360, 1265, 1160, 1075, 1060, 1030, 980 and 850 cm^{-1}.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.46; H, 9.79.

(±)-*Trans*-3aβ(*H*),7aα(*H*)-hexahydro-3α,6β-dimethyl-2(3*H*)benzofuranone (**11**).

Treating **19** (0.09 g, 0.1 mmole) in dry benzene (20 ml) with *p*-toluenesulfonic acid (0.05 g) at reflux furnished 0.070 g (90%) of **11**; ir (neat): 1770, 1440, 1431, 1372, 1325, 1305, 1254, 1220, 1180, 1121, 1092, 1045, 995, 940, 912, 840 and 705 cm^{-1}; nmr (deuteriochloroform): δ 1.02 (3H, d, J = 6 Hz, C*H*$_3$ on C-6), 1.22 (3H, d, J = 7 Hz, C*H*$_3$ on C-3), 3.76 (1H, dt, J = 10 and 4 Hz, *H*C-O).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.61; H, 9.50.

(±)-2(*R*)-[4′(*R*)-methyl-2′-oxocyclohex-(1′*S*)-yl]propionic Acid (**10**).

A solution of **19** (0.18 g, 1 mmole) in dry acetone (20 ml) was treated with Jones reagent at 0° under stirring. Completion of reaction was judged by persistant colour of reagent for 30 minutes. Acetone was removed under suction and residue diluted with ether (2 × 50 ml) and washed with water, dried over anhydrous sodium sulfate and solvent evaporated. The residue on crystallization from petroleum ether/acetone furnished 0.17 g (95%) of **10**, mp 108-109°; ir (chloroform): 3520 (weak), 3200-2800 (broad band), 1700 (strong), 1425, 1370, 1275, 1210 and 1120 cm^{-1}l nmr (deuteriochloroform): δ 1.03 (3H, d, J = 6 Hz, C*H*$_3$ on C-4′), 1.16 (3H, d, J = 7 Hz, C*H*$_3$ on C-2), 1.5-3.00 (unresolved signals), 9.1 (1H, exchanges with deuterium oxide, CO$_2$*H*).

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.31; H, 8.90.

(±)-1, 1-Diphenzyl-3(*S*)-[2′(*R*)-methylcyclohex(1′*S*)-yl]butan-1-ol (**21**).

Benzylmagnesium chloride (0.06 mole) was prepared by treating magnesium pieces (1.44 g) in dry ether (75 ml) with benzyl chloride (7.60 g). To this solution, mixture of **2**, **3** and **4** (total distilled product obtained on hydrogenation of **1**) (3.64 g, 0.02 mole) in dry ether (50 ml) was added dropwise with cooling and stirring. The reaction mixture was stirred at 0° to -5° for 1 hour and then at room temperature for 12 hours. Finally it was worked up in the manner described for the preparation of **15** earlier. The residue 6.50 g was dissolved in petroleum ether which on cooling

furnished 1.0 g of crystalline **21**, mp 143°; ir (nujol): 3400, 2995, 1495, 1445, 1405, 1315, 1300, 1125, 1075, 1090, 1030, 1005, 960, 900, 878, 840, 746 and 695 cm^{-1}; nmr (deuteriochloroform): δ 0.86 (3H, d, J = 7 Hz, CH_3 on C-4'), 1.02 (3H, d, J = 6 Hz, CH_3, on C-3), 2.57 (2H, exchanges with deuterium oxide), 2.68 (2H, m, Ar-CH_2-C-CH_2-Ar), 2.70 (1H, d, J = 14 Hz, Ar-CH_2-C-CH_2-Ar), 3.11 (1H, d, J = 14 Hz, Ar-CH_2-C-CH_2-Ar), 7.24 (5H, s, Ar*H*), 7.31 (5H, s, Ar-*H*).

Anal. Calcd. for $C_{25}H_{34}O_2$: C, 81.92; H, 9.35. Found: C, 81.87; H, 9.31.

(±)-1,1-Dibenzyl-3ξ-[2'(*R*)-hydroxy-4'(*R*)-methylcyclohex(1'*R*)-yl]butan-1-ol (**25**).

A crystalline material (0.3 g) was collected from the mother liquors left after isolating **21**; this material, on repeated crystallization from petroleum ether furnished 0.2 g of pure **25**; mp 126°; ir (nujol): 3350, 3000, 1490, 1441, 1366, 1314, 1266, 1175, 1140, 1120, 1085, 1020, 965, 925, 885, 745, 692 cm^{-1}; nmr (deuteriochloroform): δ 0.82 (3H, d, J = 7 Hz, CH_3 on C-4'), 1.02 (3H, d, J = 6 Hz, CH_3 on C-3), 2.33 (2H, exchanges with deuterium oxide), 2.65 (2H, m, Ar-CH_2-C-CH_2-Ar), 2.70 (1H, d, J = 14 Hz, Ar-CH_2-C-CH_2-Ar), 3.11 (1H, d, J = 14 Hz, Ar-CH_2-Ar), 3.61 (1H, broad s, W ½ = 6 Hz, *H*C-OH), 7.3 (5H, s, Ar-*H*), 7.35 (5H, s, Ar-*H*).

Anal. Calcd. for $C_{25}H_{34}O_2$: C, 81.92; H, 9.35. Found: C, 81.70; H, 9.51.

(±)-1,1-Dibenzyl-3(*S*)-[2'(*R*)-acetoxy-4'(*R*)-methylcyclohex-(1'*S*)-yl]butan-1-ol (**22**).

Diol **21** (0.97 g) was acetylated with acetic anhydride in presence of pyridine in usual way to furnish 1.01 g of **22**; nmr (deuteriochloroform): **d** 0.88 (3H, d, J = 7 Hz, CH_3 on C-4'), 0.96 (3H, d, J = 7 Hz, CH_3 on C-3), 1.83 (3H, s, OCOCH_3), 2.74 (4H, m, Ar-CH_2-C-CH_2-Ar), 4.96 (1H, dt, J = 10 and 4 Hz, *H*C-OCOCH_3), 7.22 (10H, s, AR*H*).

Anal. Calcd. for $C_{27}H_{36}O_3$: C, 79.37; H, 8.88. Found: C, 79.66; H, 8.95.

(±)-1-Phenyl-4(*S*)-[2'(*R*)-acetoxy-4'(*R*)-methylcyclohex-(1'*S*)-yl]pentan-2-one (**24**).

A solution of **22** (0.20 g, 0.5 mmole) in dry benzene (20 ml), iodine (0.06 g), and lead tetracacetate (0.66 g, 1 mmole) were refuxed for 24 hours. Unreacted lead tetraacetate was destroyed by adding ethylene glycol after completion of reaction. Later, the benzene layer was washed with water, 10% aqueous sodium thiosulfate solution, brine solution and dried over anhydrous sodium sulfate. Solvent removal furnished 0.126 g (80%) of crude **24**. The analytical sample was obtained by preparative tlc separation; nmr (carbon tetrachloride): δ 0.79 (3H, d, J = 7 Hz, CH_3 on C-4'), 0.91 (3H, d, J = 7 Hz, CH_3 on C-4), 1.96 (3H, s, OCOCH_3), 3.56 (2H, s, Ar-CH_2), 4.53 (4H, broad m, *H*C-OCOCH_3), 7.23 (5H, s, Ar-*H*).

Anal. Calcd. for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 75.86; H, 8.81.

(±)-*Trans*-4aβ(*H*),8aα(*H*)-octahydro-4α-7α-dimethyl-2*H*-1-benzopyran-2-one (**3**).

Compound **24** (0.055 g) on chromium trioxide oxidation furnished acetoxy acid **23**, which was saponified and the resulting hydroxy acid was cyclized (in the manner described for **11**). The product was chromatographed on alumina to furnish 0.019 g of pure **3**; nmr (deuteriochloroform): δ 0.97 (3H, d, J = 6 Hz, CH_3), 1.00 (3H, d, J = 6 Hz, CH_3), 4.14 (1H, dt, J = 10 and 4 Hz, *H*-C-O-).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.67; H, 10.03.

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