(+)-Occidentalol: Absolute Stereostructure and Total Synthesis[1]

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Hydroxy ketone **7** has been prepared from both (+)-dihydrocarvone (**3**) and (+)-occidentalol (**2**), thus establishing the absolute stereostructure of the latter. The three-stage conversion of compound **7** into (+)-occidentalol constitutes a total synthesis of the sesquiterpene.

L'hydroxycétone **7** a été préparée à partir des deux produits (+)-dihydrocarvone (**3**) et (+)-occidentalol (**2**) établissant par le fait même la stéréostructure absolue de ce dernier. La conversion en trois étapes du composé **7** en (+)-occidentalol constitue une synthèse totale du sesquiterpène.

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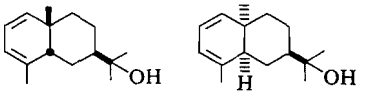
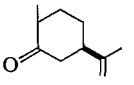
Introduction

The sesquiterpene alcohol (+)-occidentalol was first isolated from the wood of Eastern white cedar (*Thuja occidentalis* L.) by Nakatsuka and Hirose (1). Subsequent reports from various laboratories lead to the acceptance of structure **1** for this interesting sesquiterpene (2–5). In 1969, Hortmann and De Roos reported a careful analysis of the 100 MHz p.m.r. spectrum of (+)-occidentalol and suggested structure **2** (6).



1 **2**

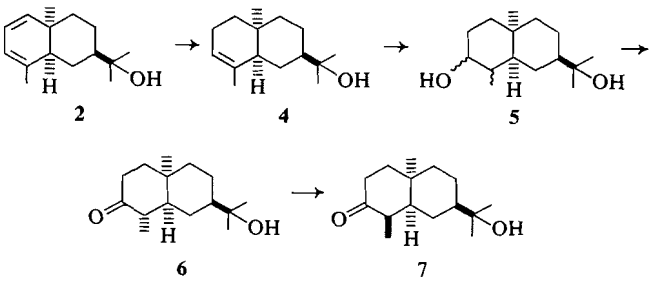
We have carried out a straightforward chemical correlation of (+)-occidentalol and (+)-dihydrocarvone (**3**) as well as a total synthesis of the sesquiterpene. Our results confirm Hortmann's structure, as well as the absolute configuration previously assigned to (+)-occidentalol on the basis of o.r.d. studies (3, 4). Since this work was completed, another synthesis of (+)-occidentalol (**7**) and one of its enantiomorph (8) have been reported.



3

Natural (+)-occidentalol, generously provided by Professor H. Erdtmann, was selectively hydrogenated to obtain dihydrooccidentalol (**4**) (3) (see Scheme 1). Hydroboration of **4** yielded a mixture of diols, **5**, which was oxidized with bispyridinechromium(VI) oxide in methylene chloride (9). The initial product, which was mostly hydroxy ketone **6**, was converted to the more stable epimer **7** upon filtration through alumina. Compound **7**, m.p. 89–90°, had $[\alpha]_D^{CHCl_3}$ −18°.

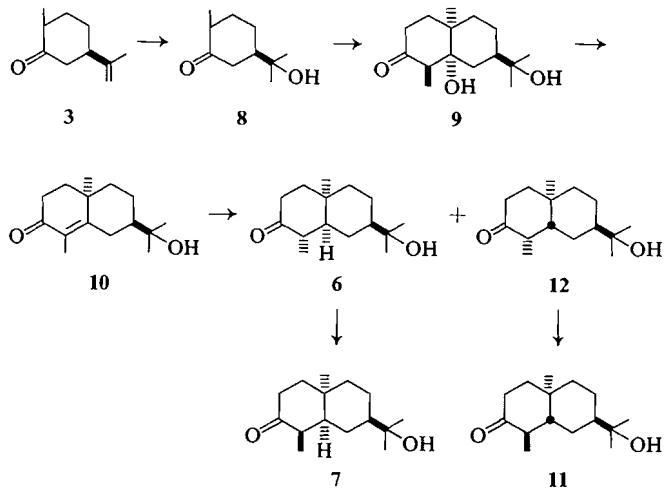
Oxymercuration–demercuration (10) of (+)-



2 **4** **5** **6** **7**

SCHEME 1

[1]Presented at the Joint Meeting of the Chemical Institute of Canada and the American Chemical Society, Toronto, Ontario, May 26, 1970.



SCHEME 2

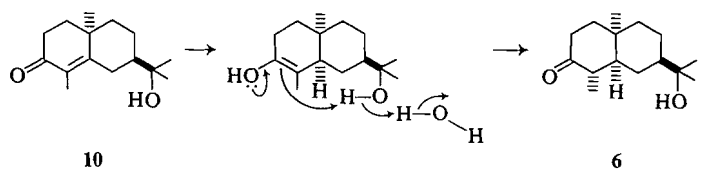
dihydrocarvone (**3**) yielded hydroxy ketone **8** (see Scheme 2). Base-catalyzed condensation of **8** with ethyl vinyl ketone gave the crystalline diol **9**, which was dehydrated to hydroxy-enone **10** by treatment with hydrogen chloride in refluxing tetrahydrofuran. The relative stereochemistry of this material, *epi*-carrisone, has been rigorously established as *trans* (11). Compound **10** was hydrogenated in methanol over palladized charcoal, yielding an oily mixture of dihydro derivatives. This crude product gave a poorly-resolved p.m.r. spectrum which was not identical to that of crystalline **7**. When a solution of the dihydro products was passed through a column of alumina, or simply stirred in contact with basic alumina, hydroxy ketone **7**, m.p. 88–89°, $[\alpha]_D^{CHCl_3}$ −16° was isolated in 32% yield.

The crude mother liquors remaining after the above treatment contained mainly *trans*-dihydro-*epi*-carrisone (**11**), an oil having $[\alpha]_D^{CHCl_3}$ +40°. Compound **11** was also obtained by reduction of *epi*-carrisone (**10**) with lithium in ammonia.

The dramatic transformation brought about by exposure to basic alumina of the oily mixture initially isolated after hydrogenation of *epi*-carrisone can be attributed to equilibration of the new axial, secondary methyl groups to their more stable epimeric positions.

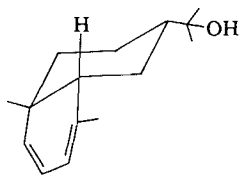
The formation of the less stable *trans*-fused epimer **12** is expected, since this results from *cis*-delivery of hydrogen. However, the initial production of the less stable epimer **6** in the *cis*-series is at first sight surprising, since this stereochemistry implies *trans*-addition of hydrogen. Overall *trans*-addition can be achieved by initial 1,4-addition, followed by kinetic protonation of the resultant enol (see Scheme 3).

A more complicated mechanism for formation of **6**, involving prior double-bond isomerization, followed by hydrogenation, was ruled out by the following experiment. Catalytic *deuteration* of **10** yielded a mixture of hydroxy ketones which was stirred with methanolic sodium methoxide to epimerize the first formed products and also to assure exchange of the α-positions. Mass spectral analysis of the recrystallized, deuterated **7** showed the presence of only a single deuterium atom, presumably at the angular position.

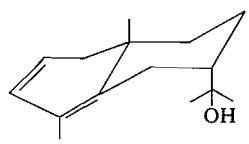


SCHEME 3

With the absolute stereostructure of (±)-occidentalol secured to our satisfaction, we set about to prepare the sesquiterpene by total synthesis. Our initial approach to the synthesis was based on a consideration of the stereochemistry of occidentalol (**2**) and its double-bond isomer **13**. Since occidentalol is a *cis*-fused decalin, it may exist in a conformation, **2***a*, in which the bulky isopropylol group occupies an equatorial position. Isomer **13**, on the other hand, is constrained to a single conformation, in which the isopropylol group is axial. From this consideration, it is clear that occidentalol

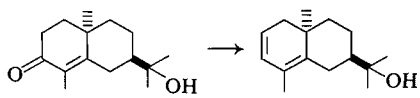


2*a*[2]



13[2]

should be more stable than isomer **13** (or the *trans*-fused isomer corresponding to **2**). It appeared attractive, therefore, to examine the isomerization of compound **13**, which was prepared in quantitative yield from *epi*-carrisone (**10**) by Shapiro's modification of the Bamford–Stevens reaction (12).



10 **13**

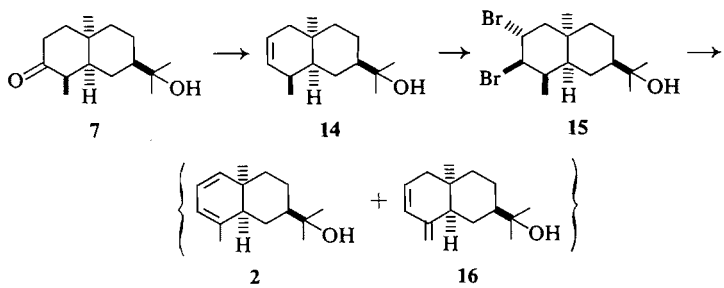
When diene **13** was treated under acidic conditions, only extensive degradation was observed. When **13** was treated with potassium *t*-butoxide in dimethylsulfoxide at 80°, there was no reaction. At 115°, some change occurred, but no occidentalol was formed (monitored by watching the δ 5.0–6.5 region in the p.m.r. spectrum, where occidentalol has a highly characteristic vinyl absorption pattern).

In order to test the stability of occidentalol itself under these conditions, it was heated with potassium *t*-butoxide in hexadeuteriodimethylsulfoxide at 80° for 50 h. After this period, the occidentalol was recovered in good yield, and extensive deuteration had occurred (20% d_3, 46% d_4, 30% d_5, and 4% d_6).

Having been thwarted in this attempt to prepare occidentalol from *epi*-carrisone, we turned to a less direct route. *cis*-Dihydro-*epi*-carrisone (**7**), prepared as outlined above, was subjected to the modified Bamford–Stevens reaction (12), to obtain the crystalline unsaturated alcohol **14** in 75% yield (see Scheme 4). This olefin reacted with bromine in CCl_4 to yield a dibromide (**15**, quantitative yield), which was dehydrobrominated by heating in 2,6-lutidine at 135° for 1 h. The product, obtained in 83% yield, was a mixture of (+)-occidentalol (**2**) and its isomer **16**, in a ratio of 55:45. The synthetic (+)-occidentalol, $[\alpha]_D^{CHCl_3}$ +313°, was indistinguishable from natural (+)-occidentalol by p.m.r., i.r., and v.p.c. mobility. The structure of isomer **16** was assigned on the basis of its spectra and empirical formula ($C_{15}H_{24}O$), determined by high resolution mass spectrometry.

The dehydrobromination of dibromide **15** was also accomplished with ethanolic KOH and with pyridine; similar ratios of **2** and **16** were obtained. Lithium dimethylpiperidide in hexane converted dibromide **15** back into olefin **14**.

Although the ratio of **2** to **16** was not changed



7 **14** **15**

2 **16**

SCHEME 4

[2]Enantiomeric projections have been used to more clearly illustrate the stereochemical point being made.

upon heating the mixture with potassium *t*-butoxide in dimethylsulfoxide, the percentage of occidentalol in the mixture did increase when it was treated in refluxing tetrahydrofuran with a trace of HCl. However, quantitative v.p.c. showed that this enhancement resulted from preferential destruction of **16**, rather than from conversion of **16** to **2**.

Experimental

All melting points are uncorrected. All p.m.r. spectra were measured on a Varian T-60 spectrophotometer.[3] Chemical shifts are given in p.p.m. downfield from internal tetramethylsilane. The i.r. spectra were measured on Perkin–Elmer 137 and 237 Infrared Spectrophotometers. Mass spectra were determined on a Consolidated 110 High Resolution Mass Spectrometer. Microanalyses were performed by the University of California Microanalytical Laboratory, Berkeley, California.

7β-(2-Hydroxy-2-propyl)-1,4aα-dimethyl-8aα-decahydronaphth-2-ol (5)

Dihydrooccidentalol (**4**) prepared by the method of von Rudloff and Erdtmann (3), was hydroborated by the method of Zweifel and Brown (13). From 1.9 g of unsaturated alcohol **4** was obtained 1.74 g of diol **5** (90% yield). The non-crystalline mixture was used directly in subsequent transformations.

7β-(2-Hydroxy-2-propyl)-1β,4aα-dimethyl-3,4,4a,5,6,7,8aα-octahydronaphthalen-2(1H)-one (7)

To a magnetically-stirred solution of 200 mg diol mixture **5** in 8.5 ml dry methylene chloride was added in one portion 430 mg red bispyridinechromium(VI) oxide (9). After stirring for 5 min, the supernatant liquid was decanted and the dark, tarry residue remaining was washed twice with 10 ml portions of ether. The combined organic fractions were washed successively with dilute, aqueous NaOH, dilute hydrochloric acid, and saturated brine. After drying over anhydrous $MgSO_4$, the solvent was removed to obtain 104 mg yellow oil, which gave a poorly resolved p.m.r. spectrum. Several rapid filtrations of a CCl_4 solution of this material through neutral alumina afforded 65 mg of a colorless oil which crystallized upon standing. The p.m.r. spectrum of this crystalline material was well resolved and completely different from that of the crude product. Recrystallization from hexane yielded material of analytical purity, m.p. 89–90°, $[\alpha]_D^{CHCl_3}$ −18°. The p.m.r. in CCl_4: δ 0.19 (C-1 Me, d, $J = 7$ Hz), 1.11 (*i*-propyl Me, s), 1.31 (angular Me, s); i.r. in CCl_4: 3400, 1700 cm^{-1}.

Anal. Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.40; H, 11.11.

(+)-5β-(2-Hydroxy-2-propyl)-2α-methylcyclohexanone (8)

A 50 g sample of (+)-dihydrocarvone (**3**) was added in one portion to a stirred solution of 104 g mercuric acetate in 360 ml water and 360 ml THF (10). Characteristic decolorization occurred after 20 s. After 7 min, 360 ml of 3 *M* aqueous NaOH was added, followed by 360 ml 0.3 *M* $NaBH_4$ in 3 *M* aqueous NaOH.[4] The product was isolated in the normal way by extraction into ether. After stirring over 20 g basic alumina (to remove the residual, finely dispersed mercury), the solvent was removed to obtain 52 g (93%) of keto alcohol **8** as a colorless oil, which was used without further purification. The p.m.r. in CCl_4: δ 0.97 (Me, d, $J = 6$ Hz), 1.18 (*i*-propyl Me, s).

8aα-Hydroxy-7β-(2-hydroxy-2-propyl)-1β,4aα-dimethyloctahydronaphthalen-2(1H)-one (9)

To a well-stirring solution of 52 g ketone **8** in 110 ml ether at 0°, under nitrogen, was added a solution of 3.8 g KOH in 12 ml 95% ethanol. After 10 min, 13 g ethyl vinyl ketone in 75 ether was added dropwise over a period of 1 h. Stirring was continued at 0° for an additional 1 h, then at 25° for 1.5 h, during which time considerable quantities of product **9** precipitated. The reaction mixture was concentrated to approximately one-half volume (vacuum) and the resulting precipitate isolated by filtration.[5] The solid was taken up in ethyl acetate, washed twice with water and once with brine. The aqueous washes were extracted once with ether and the organic portions were combined. The solvent was evaporated from the crude solution on a steam bath at atmospheric pressure until crystals began to appear. Compound **9** was obtained as colorless needles, m.p. 189–190°. The yield was 13.0 g (31%). The p.m.r. in CH_3OH: δ 0.99 (Me, s), 1.02 (Me, d, $J = 7$ Hz), 1.10 (Me, s); i.r. in KBr: 3500, 1690 cm^{-1}.

Anal. Calcd. for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.55; H, 10.15.

7β-(2-Hydroxy-2-propyl)-1β,4aα-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (epi-Carrisone (10))

A solution of 27 g keto-diol **9** in 600 ml THF was treated with 10 ml concentrated hydrochloric acid. After refluxing for 2 h, the solution was cooled and concentrated to 100 ml under reduced pressure. The concentrated solution was diluted with 400 ml ether and washed with 30% aqueous NaOH until the aqueous phase remained basic. After back-extraction of the aqueous washes with ether, the combined organic phases were washed with brine, dried, and evaporated under reduced pressure. The resultant oil was seeded with crystalline *epi*-carrisone, which had been previously obtained by chromatography of 6.5 g of the crude product (11). The solid obtained in this way was recrystallized from hexane – ethyl acetate to give 18.5 g (74% yield) of crystalline ketone **10**, m.p. 54–56° (lit. (13) m.p. 56°). The n.m.r. in CCl_4: δ 1.12 (angular Me, s), 1.22 (Me, s), 1.23 (Me, s), 1.74 (vinyl Me, s); i.r. in CCl_4: 3400, 1660 cm^{-1}.

[3]We thank the Dupont Company and the Research Committee, Berkeley Division, University of California, for the purchase of this instrument.

[4]Brown and Geohagen's procedure (10) calls for 0.5 *M* $NaBH_4$ in 3 *M* aqueous NaOH. However, some carbonyl reduction was observed when such a concentration was utilized in the present experiment.

[5]When these original mother liquors were washed several times with water and the volatile material evaporated under reduced pressure, a residue containing mostly ketone **8** was obtained. This oil could be resubmitted to the annelation reaction with ethyl vinyl ketone to give better yields of keto-diol **9** (greater than 50%) than were obtained using pure **8**.

TABLE 1. Catalytic hydrogenation of *epi*-carrisone

Run	Catalyst/solvent	Product ratio (7/11)	Method of analysis
(1)	10% Pd–C/95% ethanol	3:2	p.m.r.*
(2)	10% Pd–C/95% ethanol with a trace of KOH	1:1	p.m.r.*
(3)	10% Pd–C/ethyl acetate	2:1‡	p.m.r.;* v.p.c.†
(4)	10% Pd–C/acetic acid	4:1§	v.p.c.
(5)	10% Pd–C/95% ethanol with a trace of HCl	2:1	p.m.r.*
(6)	10% Pd–C/methanol	3:2	p.m.r.*
(7)	10% Pd–C/methanol with 5% (by weight) acidic Al_2O_3	3:1§	p.m.r.*
(8)	Rh–Al_2O_3/hexane	1:4§	p.m.r.*
(9)	Pt–C/95% ethanol	Complex mixture‖	p.m.r.*

*Estimates of *cis* to *trans* ratios were made by comparison of the relative areas of the isopropyl methyl peaks at δ 1.11 and 1.19, respectively.

†The v.p.c. analyses were made on the previously trimethylsilylated compounds.

‡This run gave 40% reduction of the carbonyl, which was not included in the *cis*/*trans* ratio.

§Although hydrogenation in acetic acid (run 4) gave the maximum *cis*/*trans* ratio, experience has shown that for ease of work-up and for optimum recovery of pure, crystalline *cis* isomer **7**, reduction in methanol with acidic alumina (run 7) is the method of preference.

‖This mixture probably includes products resulting from reduction of the carbonyl and hydrogenolysis.

7β-(2-Hydroxy-2-propyl)-1β,4aα-dimethyl-3,4,4a,5,6,7,-8,8aα-octahydronaphthalen-2(1H)-one (cis-Dihydro-epi-carrisone (7)) and 7β-(2-Hydroxy-2-propyl)-1β,4aα-dimethyl-3,4,4a,5,6,7,8,8aβ-octahydronaphthalen-2(1H)-one (trans-Dihydro-epi-carrisone (11))

A 4.79 g sample of *epi*-carrisone (**10**) in 100 ml absolute methanol was hydrogenated at atmospheric pressure over a mixture of 1.2 g acidic alumina and 0.2 g 10% palladium-on-carbon. Consumption of hydrogen ceased abruptly after the uptake of 1 *M* equiv. (500 ml hydrogen in 50 min). The reaction mixture was filtered and 2 ml water added to hydrolyze a small amount of methyl ketal (comprising about 5% of the product, as estimated by p.m.r.), which was observed to have formed in previous runs. After 2.5 h at room temperature, the reaction mixture was concentrated to 10 ml and partitioned between water and ether. The organic layer was washed with brine, dried, and evaporated. The crude crystalline product was obtained in quantitative yield. The crude material was shown by v.p.c. analysis to consist of a 3:1 mixture of *cis* and *trans*-dihydro-*epi*-carrisones (**7** and **11**, respectively). This conclusion was corroborated by comparison of the relative peak heights of the respective isopropylol methyl groups of **7** and **11** in the p.m.r. spectrum of the mixture (δ 1.11 for **7**, 1.19 for **11**).

By a combination of column chromatography (silica gel) and fractional crystallization, crystalline **7** was obtained; 2.09 g (43% yield), m.p. 88.5–89.5°, $[\alpha]_D^{CHCl_3}$ −18°. This material was identical by p.m.r., i.r., v.p.c. retention time, mixture m.p. and optical rotation with ketol prepared from (+)-occidentalol.

Anal. Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 57.83; H, 10.98.

The structure assignment for the other product of this hydrogenation, **11**, was made on the basis of its p.m.r. spectrum, which was superimposable upon the p.m.r. spectrum of an authentic sample of **11** (see below), and its indistinguishability from authentic **11** by v.p.c.

Various other hydrogenation conditions were explored and are summarized in Table 1.

7β-(2-Hydroxy-2-propyl)-1β,4aα-dimethyl-3,4,4a,5,6,7,-8,8aβ-octahydronaphthalen-2(1H)-one (trans-Dihydro-epi-carrisone (11))

A solution of 0.4 g *epi*-carrisone (**10**) in 3 ml dry THF was added in one portion to 0.025 g lithium metal dissolved in 20 ml ammonia (freshly distilled from sodium). After 50 min, enough ammonium chloride was added to discharge the blue color, followed by enough dilute aqueous hydrochloric acid to acidify the solution to litmus. The mixture was extracted several times with ether and the combined ether extracts were washed with brine, dried, and evaporated under reduced pressure. *trans*-Dihydro-*epi*-carrisone was obtained as an oil; 0.353 g (88%). The analytical sample was obtained by preparative v.p.c. on a Carbowax column. The analytically pure material could not be crystallized from various proportions of ethyl acetate and hexane; $[\alpha]_D^{CHCl_3}$ +40°; p.m.r. in CCl_4: δ 0.95 (Me, d, J = 6 Hz), 1.08 (Me, s), 1.19 (*i*-propyl Me, s); i.r. in CCl_4: 3400, 1680 cm^{-1}.

Anal. Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.85; H, 10.75.

7β-(2-Hydroxy-2-propyl)-1,4aα-dimethyl-4,4a,5,6,7,8-hexahydronaphthalene (13)

A 0.20 g sample of *epi*-carrisone (**10**) (11) 0.16 g *p*-toluenesulfonylhydrazide, and 1 drop concentrated hydrochloric acid was added to 10 ml tetrahydrofuran and the mixture was refluxed for 30 h. The mixture was then diluted with 10 ml benzene and distilled until all the tetrahydrofuran and benzene–water azcotrope had been collected and the b.p. had reached 80°. The remaining solution was cooled to 0°, under nitrogen, and diluted with 5 ml dry tetrahydrofuran. Ethereal methyllithium was added (1.8 ml of a 1.6 *M* solution), and the red reaction mixture was stirred for 2 h at room temperature. Excess methyllithium was de-

stroyed by the addition of 10 ml water, and the layers were separated. The aqueous layer was extracted several times with pentane. After drying, the combined organic solutions were evaporated to yield 0.19 g (99% yield) of diene **13**, as a slightly yellow oil, which was used directly without further purification. The p.m.r. in CCl_4: δ 0.91 (angular Me, s), 1.07 (Me, s), 1.13 (Me, s), 1.71 (vinyl Me, s); i.r. in CCl_4: 3400 cm^{-1}.

7β-(2-Hydroxy-2-propyl)-1β,4aα-dimethyl-1,4,4a,5,6,7,8,-8aα-octahydronaphthalene (14)

A 0.200 g sample of *cis*-dihydro-*epi*-carrisone (**7**) (1) in 20 ml tetrahydrofuran together with 0.147 g *p*-toluenesulfonylthydrazide and 2 drops concentrated hydrochloric acid was refluxed for 7 h on a steam bath. The nearly colorless reaction mixture was cooled and washed twice with 2 ml portions of saturated brine. The organic layer was diluted with 10 ml ether and 20 ml benzene and distilled until the b.p. reached 80°. The reaction flask was sealed with serum stoppers, cooled to 0°, and 5 ml of tetrahydrofuran was introduced. Ethereal methyllithium (3 ml of a 1.6 *M* solution) was added by syringe and the mixture was kept for 10 min at 0°. The cooling bath was then removed and the mixture was stirred at room temperature for 2.5 h, at which time gas evolution had ceased. The resultant brown mixture was treated cautiously with 5 ml water and then 3 ml pentane. The phases were then separated and the aqueous portion extracted twice with pentane. The combined organic phases were dried and evaporated to obtain 0.190 g of a lightly colored glass. Chromatography on 7 g silica gel yielded 0.138 g unsaturated alcohol **14** (75% yield) as a white solid, m.p. 75.5–76.5°, $[\alpha]_D^{CHCl_3}$ +54°; p.m.r. in CCl_4: δ 0.90 (Me, s), 0.95 (Me, d, J = 7 Hz), 1.08 (*i*-propyl Me, s), 5.25 (H-2 and -3, unresolved m); i.r. in CCl_4: 3400 cm^{-1}.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.77; H, 11.84.

2β,3α-Dibromo-7β-(2-hydroxy-2-propyl)-1β,4aα-dimethyl-8aα-decahydronaphthalene (15)

To a 0.42 g sample of unsaturated alcohol **14** in 20 ml carbon tetrachloride at 0° was added a solution of 0.35 g bromine in 1 ml carbon tetrachloride. The reaction mixture was stirred for 2.5 h at 0°. The cooling bath was then removed and 0.5 ml water and sufficient sodium hydrogen sulfite to quench the excess bromine were added. The mixture was diluted with 50 ml pentane and washed with 5 ml portions of water, saturated aqueous sodium bicarbonate and brine. After drying and evaporation at reduced pressure, dibromide **15** was obtained in quantitative yield (0.75 g). The p.m.r. in CCl_4: δ 1.11 (*i*-propyl Me, s), 1.13 (Me, d, J = 7 Hz), 1.33 (Me, s), 4.58 (CBr—*H*, m, $w_{1/2}$ = 10 Hz), 4.97 (CBr—*H*, m, $w_{1/2}$ = 10 Hz); i.r. in CCl_4: 3300 cm^{-1}. This crude product was used in the succeeding transformation with further purification.

(+)-7β-(2-Hydroxy-2-propyl)-1,4aα-dimethyl-4a,5,6,7,8,-8aα-hexahydronaphthalene ((+)-occidentalol (2)) and 7β-(2-Hydroxy-2-propyl)-4aα-methyl-1-methylene-1,4,4a,5,6,7,8,8aα-octahydronaphthalene (16)

A solution of 0.626 g dibromide **15** in 9 ml freshly distilled 2,6-lutidine was heated in an oil bath at 133–135° for 1 h. During the heating period, the mixture darkened and lutidine hydrobromide precipitated. The reaction mixture was cooled to room temperature and decanted. After washing the solid residue with 40 ml of pentane, the combined organic solutions were diluted with more pentane to a total volume of 70 ml. The solution was washed with 15% aqueous hydrochloric acid until the wash remained acidic (five 10 ml portions), and the combined aqueous washes were extracted with pentane. The organic fractions were combined, washed with 5 ml 0.1 *M* aqueous NaOH, dried, and evaporated. The product was 0.298 g (82.5%) of pale yellow semi-solid, shown by v.p.c. analysis (3 ft × 1/4 in. Carbowax, 190°) to be a 55:45 mixture of (+)-occidentalol (**2**) and its isomer **16**. Analytical samples were obtained by preparative v.p.c. on the aforementioned column.

The synthetic (+)-occidentalol so obtained was identical to natural (+)-occidentalol by p.m.r. and i.r. spectroscopy and by v.p.c. and t.l.c. mobility. The synthetic material, collected by preparative v.p.c., melted over the range 86.5–92° (lit. (3) 97.5–98°, 95.2–95.6°). The m.p. of an authentic sample of (+)-occidentalol, generously supplied to us by Professor Erdtmann, m.p. 92–93°, was not depressed in admixture with the synthetic material. Our synthetic (+)-occidentalol had $[\alpha]_D^{CHCl_3}$ +313° (lit. (3) $[\alpha]_D^{CHCl_3}$ +361°). The authentic sample supplied us by Professor Erdtmann had $[\alpha]_D^{CHCl_3}$ +327°.

Anal. *m/e* for $C_{15}H_{24}O$: 220.1830.

The structural assignment for the isomeric product was made on the basis of its empirical formula, p.m.r. spectrum and i.r. spectrum; $[\alpha]_D^{CHCl_3}$ −67.7°; p.m.r. in CCl_4: δ 0.83 (Me, s), 1.14 (*i*-propyl Me, s), 4.71 (=CH_2, m); i.r. in CCl_4: 3400 cm^{-1}.

Anal. *m/e* for $C_{15}H_{24}O$: 220.1843.

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