Experimental Section

Melting points were determined on a Reichert micro hotstage and are uncorrected. Infrared spectra of CCl_4 solutions were recorded on an Acculab 5 spectrophotometer, and ^1H NMR spectra of $CDCl_3$ solutions (Me_4Si, $\delta = 0$ ppm) were obtained on a Varian EM 390 spectrometer. The ^{13}C NMR spectra of $CDCl_3$ solutions were run on a Nicolet NT-200, wide-bore, broad-band spectrometer, operating with an Oxford magnet at 50.31 MHz in the Fourier transform mode. The carbon shifts on formula **5** are in ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm.

18-Acetoxy-13β-devinyl-13β-carboxypimarene (1d). Osmium tetroxide, 1.00 g (4 mmol), was added slowly to a stirring solution of 1.32 g (4 mmol) of 18-acetoxypimaradiene (**1a**)[1] in 60 mL of dioxane, and the stirring was continued for 24 h. A stream of hydrogen sulfide gas was passed through the mixture for 1 h and the latter filtered through Celite. The filtrate was evaporated under vacuum and the resultant residue chromatographed on silica gel. Elution with 50:1 chloroform–methanol yielded 900 mg of amorphous diol **1b**: ^1H NMR δ 0.76, 0.86, 0.86 (s, 3 each, methyls), 2.04 (s, 3, COMe), 3.5–4.0 (m, 5, 2 OCH_2, OCH), 5.0–5.3 (m, 1, olefinic H).

A solution of 1.00 g of periodic acid dihydrate and 900 mg of diol **1b** in 50 mL of tetrahydrofuran was stirred for 1 h. Water, 10 mL, was added and the mixture extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated, yielding 818 mg of liquid aldehyde **1c**: ^1H NMR δ 0.73, 0.86, 1.03 (s, 3 each, methyls), 2.08 (s, 3, COMe), 3.77 (q, 2, J = 13 Hz, OCH_2), 5.28 (br s, 1, olefinic H), 9.48 (s, 1, CHO).

A solution of 2.5 mmol of Jones reagent (prepared from a solution of 70 g of chromium trioxide in 500 mL of water and 61 mL of concentrated sulfuric acid) was added slowly to a stirring solution of 818 mg of aldehyde **1c** in 80 mL of acetone at room temperature. After 0.5 h the mixture was decomposed with 5% sodium bisulfite solution, diluted with 150 mL of water, and extracted exhaustively with chloroform. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue on silica gel and elution with 25:1 chloroform–methanol gave 570 mg of solid whose crystallization from hexane afforded crystalline acid **1d**: mp 93–95 °C; ^1H NMR δ 0.75, 0.86, 0.90 (s, 3 each, methyls), 2.08 (s, 3, COMe), 3.71 (q, 2, J = 11 Hz, OCH_2), 5.35 (br s, 1, olefinic H).

Anal. Calcd for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.45; H, 9.40.

Methyl 18-Acetoxy-13β-devinylpimarene-13β-acetate (1f) and 14α-Methoxy-15-hibone (2). A solution of 570 mg of acid **1d** in 5 mL of oxalyl chloride was stirred at room temperature under nitrogen for 2 h, and then the excess reagent was removed by vacuum distillation. A solution of the residue in 30 mL of dry ether was added over a 1-h period to a stirring solution of 3 mmol of diazomethane in 30 mL of anhydrous ether, containing 1.8 mL of triethylamine, at 0 °C under nitrogen, and the stirring was continued at room temperature for 2 h. The mixture was filtered and the filtrate evaporated under vacuum, leaving 627 mg of semisolid diazo ketone **1e**: IR 2100 (C=N_2, s), 1725 (C=O, s), 1636 ($COCN_2$, s) cm^{-1}; ^1H NMR δ 0.77, 0.89, 1.15 (s, 3 each, methyls) 2.05 (s, 3, COMe), 3.75 (q, 2, J = 9 Hz, OCH_2), 5.28 (br s, 1, olefinic H), 5.46 (s, 1, CHN_2).

Silver oxide, 0.3 g, was added in portions to a stirring solution of 627 mg of diazo ketone **1e** in 30 mL of anhydrous methanol at 60 °C, and the stirring was continued at this temperature for 2 h. The mixture was filtered and the filtrate evaporated under vacuum. The organic residue, 485 mg, was chromatographed on silica gel. Elution with 50:1 benzene–ethyl acetate gave first 256 mg of amorphous ester **1f**: IR 1738 (C=O, s) cm^{-1}; ^1H NMR δ 0.80, 0.89, 1.04 (s, 3 each, methyls), 2.05 (s, 3, COMe), 2.61 (s, 2, $COCH_2$), 3.11 (s, 3, OMe), 3.74 (q, 2, J = 9 Hz, OCH_2), 5.21 (br s, 1, olefinic H).

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 73.62; H, 9.31.

Further elution led to 102 mg of solid, whose crystallization from methanol yielded crystalline keto ester **2**: mp 118–120 °C.

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 73.71; H, 9.25.

Acknowledgment. P.C. and M.C. acknowledge gratefully support for the work in Perugia by the Ministero Pubblica Istruzione. B.P. and E.W. are indebted to Banavara L. Mylari for the initial observation of the unusual reaction.

Registry No. **1a**, 1686-60-8; **1c**, 89710-39-4; **1d**, 89710-40-7; **1e**, 89710-41-8; **1f**, 89710-42-9; **2**, 89710-43-0.

(8) Duc, D. K. M.; Fétizon, M.; Lazare, S.; Grant, P. K.; Poisson, J.; Bernassau, J.-M.; Roque, N. F.; Wovkulish, P. M.; Wenkert, E. *Tetrahedron* **1981**, *37*, 2371. The C(18) shift of hibane (**6a**), recorded therein, should read "33.7 ppm".

Carbon–Carbon Bond Formation by the Reduction of Dienic Esters

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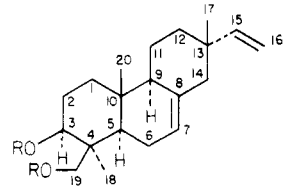
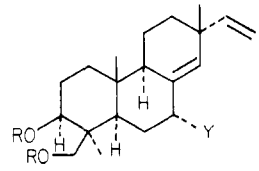
In an attempt of conversion of the isopimaradiene structure of the virescenols[1] into that of a sandaracopimaradiene system, i.e., moving the nuclear double bond from the Δ^7 to the $\Delta^{8(14)}$ position, an oxidation–reduction pathway was chosen. The reduction phase of the transformation took an unusual course, whose observation is the subject of the present report.

Photooxygenation of virescenol B diacetate (**1a**) has been shown to move the nuclear olefinic linkage to the $\Delta^{8(14)}$ location.[2] When on tosylation of the oxidation product

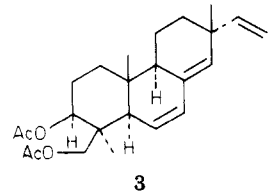


1a, R = Ac
b, R = H

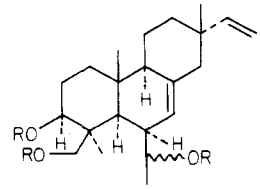


2a, R = Ac, Y = OH
b, R = Y = H

2a (for subsequent C-7 deoxygenation) the allylic alcohol underwent dehydration, the resultant diene **3** was exposed to reduction by lithium in ammonia. The reaction yielded three products, two of which were obtained in 42% yield in the form of a difficultly separable, ca. 2:1 mixture of virescenol B (**1b**) and its $\Delta^{8(14)}$ isomer **2b** and could be converted on acid treatment into a single isomer, the $\Delta^{8(9)}$ compound.[1] The major product, isolated in 47% yield, was a triol in which a hydroxyethyl group had been attached to the virescenol B skeleton. Structure **4a** could be as-



3



4a, R = H
b, R = Ac

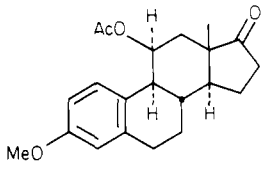
(1) Polonsky, J.; Baskevitch, Z.; Cagnoli Bellavita, N.; Ceccherelli, P. *Bull. Soc. Chim. Fr.* **1970**, 1912.

(2) Ceccherelli, P.; Curini, M.; Tingoli, M.; Pellicciari, R. *Gazz. Chim. Ital.* **1978**, *108*, 129.

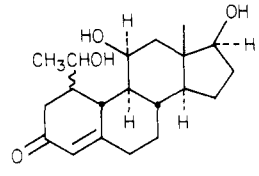
0022-3263/84/1949-2054$01.50/0

signed to the product on the assumption of the reduction having initiated at the site of the 19-acetoxy group, the ketyl having added intramolecularly to the diene at C(6), and the resultant allyl radical having accepted a hydrogen atom at C(14) from the cosolvent tetrahydrofuran.[3] Furthermore, a second reduction must have taken place on the carbonyl carbon of the new 6β-acetyl group upon its being unmasked from its hemiketal lithio salt.[4] The ^{1}H NMR spectrum of the triacetate **4b** confirmed the unusual structure.

The intramolecular, reductive transfer of acetyl groups from ester side chains onto nuclear carbon sites has precedent in the steroid field. Thus the Birch reduction of estrone and cortisone derivatives **5** and **7**, respectively, have been reported to lead to products **6**[5] and **8**,[6] respectively.



5



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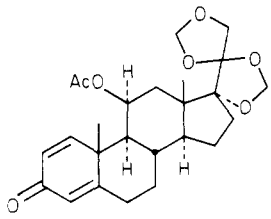

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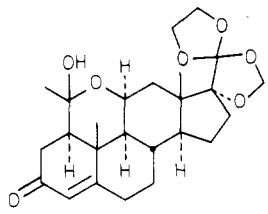
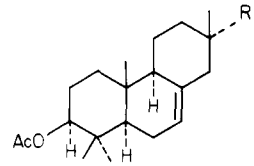


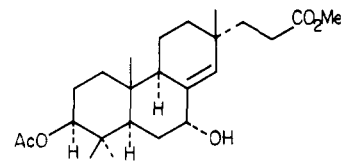
8

The ease of the new carbon–carbon bond-forming reaction in the dienic ester reduction (**3** → **4a**) suggested its use for natural products synthesis. The following discussion illustrates an example of its application in the conversion of a diterpene into a steroid skeleton.[7]

Hydroboration of 19-deoxyvirescenol acetate (**9a**),[8] followed by alkaline hydrogen peroxide oxidation, yielded alcohol **9b**, whose Jones oxidation afforded acid **9c**. Homologation of the latter by the Arndt–Eistert method gave ester **9d**, whose photooxygenation,[2] followed by the reduction of the resultant hydroperoxide by sodium iodide, led to hydroxy ester **10**. Dehydration of the latter with *p*-toluenesulfonyl chloride and pyridine resulted in the formation of dienic ester **11**.



9a, R = $CH{=}CH_2$
b, R = $(CH_2)_2OH$
c, R = CH_2CO_2H
d, R = $(CH_2)_2CO_2Me$



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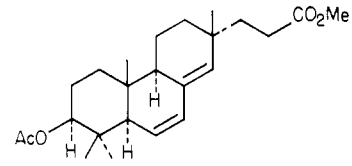
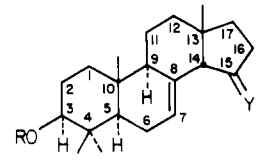
Reduction of ester **11** with lithium in ammonia yielded tetracyclic diol **12a** and its acetate **12b**,[9] whose oxidation



11



12a, R = H; Y = α-H, β-OH
b, R = Ac; Y = α-H, β-OH
c, R = Ac; Y = O

with Collins reagent gave keto ester **12c**. The stereochemistry of the reductive ring closure had taken place in a cis manner, as the ^{13}C NMR analysis of the diol **12a** and the keto ester **12c**, based on proper models,[7] indicated.

Experimental Section

Melting points were determined on a Reichert micro hotstage and are uncorrected. Infrared spectra of $CHCl_3$ solutions were recorded on an Acculab 5 spectrophotometer, and ^{1}H NMR spectra of $CDCl_3$ solutions (Me_4Si, δ = 0 ppm) were obtained on a Varian EM 390 spectrometer. The ^{13}C NMR spectra of $CDCl_3$ solutions were run on a Nicolet NT-200, wide-bore, broad-band spectrometer, operating with an Oxford magnet at 50.31 MHz in the Fourier transform mode. The carbon shifts are in ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. All chromatographic separations were carried out on silica gel and all extracts dried over anhydrous Na_2SO_4.

7,8-Dihydro-6,7,8,14-didehydrovirescenol B Diacetate (3). A solution of 500 mg of hydroxy acetate **2a**[2] and 1.00 g of *p*-toluenesulfonyl chloride in 20 mL of dry pyridine was kept at room temperature for 24 h and then poured into water and extracted with chloroform. The extract was washed with 2% sulfuric acid solution, saturated sodium bicarbonate solution, and water. It then was dried and evaporated. Chromatography of the residue and elution with 50:1 benzene–ethyl acetate led to 350 mg of amorphous, colorless triene **3**:[10] ^{1}H NMR δ 0.75, 1.00, 1.03 (s, 3 each, methyls), 2.00, 2.00 (s, 3 each, Ac methyls), 4.06, 4.18, 4.30, 4.42 (four-line AB, 2, 2 H-19), 4.64 (m, 1, H-3), 5.30 (br s, 1, H-14), 5.70 (dd, 1, J = 10, 2 Hz, H-7), 5.90 (dd, 1, J = 10, 4 Hz, H-6), 4.8–5.9 (m, 3, vinyl Hs).

Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.72; H, 8.61.

Reduction of Olefinic Ester 3. A solution of 1.00 g of ester **3** in 30 mL of tetrahydrofuran was added slowly to a stirring solution of 200 mg of lithium in 150 mL of liquid ammonia under nitrogen at −40 °C, and the mixture was then stirred for 45 min. Enough ammonium chloride was added to discharge the blue color and the ammonia allowed to evaporate. The residue was shaken with a mixture of water and chloroform and the organic layer dried and evaporated. Chromatography of the residue and elution with 20:1 chloroform–methanol led first to 330 mg of a difficultly separable, 2:1 mixture of virescenol B (**1b**)[1] and 8,14-dehydro-7,8-dihydrovirescenol B [^{1}H NMR δ 0.80, 0.85, 1.23 (s, 3 each, methyls)]. Exposure of a solution of 100 mg of the mixture in 100 mL of dry chloroform to gaseous hydrogen chloride for 3 days at room temperature yielded 98 mg of isovirescenol B,[1] spectrally

(3) In the absence of more data this reaction path is indistinguishable from the electron acceptance by the diene, intramolecular carbon–carbon bond formation between the diene anion radical and the 19-acetoxy carbonyl group, and hydrogen capture by the resultant allyl radical from tetrahydrofuran.

(4) The hydroxyethyl group possessing the unique 6β configuration is the consequence of the site of the origin of the acetyl group transfer having been a 4β substituent. The fact of the triol being a single stereoisomer and the new carbinol carbon having unique stereochemistry is more difficult to explain. The 6β-acetyl precursor of triol **4a** is restricted to a conformation in which the ketonic side chain lies in a plane encompassing its two carbons and oxygen and C(6) and C(8), i.e., parallel to the plane incorporating carbons 4, 10, 19, and 20. Whereas this steric constraint permits the 6β-acetyl group two energetically preferred rotamer populations, one must be highly preponderant to permit the formation of a single secondary alcohol in a reduction limited to hydrogen delivery exclusively from the side away from the axial C(4) and C(10) substituents (cf. Aranda, G.; Bernassau, J.-M.; Fétizon, M. *J. Org. Chem.* **1977**, *42*, 4256).

(5) Magerlein, B. J.; Hogg, J. A. *J. Am. Chem. Soc.* **1958**, *80*, 2220.

(6) Tanaba, M.; Chamberlin, J. W.; Nishiura, P. Y. *Tetrahedron Lett.* **1961**, 601.

(7) For a recent diterpene–steroid transformation, see: Wenkert, E.; Davis, L. L.; Mylari, B. L.; Solomon, M. F.; da Silva, R. R.; Shulman, S.; Warnet, R. J.; Ceccherelli, P.; Curini, M.; Pellicciari, R. *J. Org. Chem.* **1982**, *47*, 3242.

(8) Ceccherelli, P.; Curini, M.; Tingoli, M.; Pellicciari, R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1924.

(9) The uncyclized, monoolefinic, primary alcohol reduction products were not isolated.

(10) This compound has been prepared previously by other means: Ceccherelli, P.; Curini, M.; Pellicciari, R. *Gazz. Chim. Ital.* **1981**, *111*, 509.

identical with an authentic sample.

Further elution gave 430 mg of solid whose crystallization from methanol afforded colorless, crystalline triol **4a**: mp 180–182 °C; ^{1}H NMR δ 0.82, 0.91, 1.41 (s, 3 each, methyls), 1.22 (d, 3, J = 6 Hz, Me of hydroxyethyl), 3.10 (m, 1, H-3), 4.25 (m, 1, OCH of hydroxyethyl), 4.41 (s, 2, 2 H-19), 5.50 (d, 1, J = 6 Hz, H-7), 4.7–5.9 (m, 3, vinyl Hs).

Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41. Found: C, 75.60; H, 10.65.

6β-(α-Acetoxyethyl)virescenol Diacetate (4b). A solution of 100 mg of triol **4a** and 1 mL of acetic anhydride in 2 mL of pyridine was kept at room temperature for 24 h and the mixture then worked up in the usual manner. Chromatography of the crude product, 100 mg, and elution with 20:1 benzene–ethyl acetate yielded 90 mg of a solid whose crystallization from methanol gave colorless, crystalline triacetate **4b**: mp 132–134 °C; ^{1}H NMR δ 0.90, 0.99, 1.20 (s, 3 each, methyls), 2.00, 2.03, 2.06 (s, 3 each, Ac methyls), 3.88, 4.02, 4.65, 4.79 (four-line AB, 2, 2 H-19), 4.50 (m, 1, H-3), 5.31 (m, 1, OCH of acetoxyethyl), 5.50 (d, 1, J = 6 Hz, H-7), 4.8–6.0 (m, 3, vinyl Hs).

Anal. Calcd for $C_{28}H_{42}O_6$: C, 70.85; H, 8.92. Found: C, 70.65; H, 8.71.

3β-Acetoxy-15,16-dihydroisopimaradien-16-ol (9b). A 1 M solution of borane–tetrahydrofuran complex in 4 mL of tetrahydrofuran was added to a stirring solution of 2.50 g of 3β-acetoxyisopimaradiene (**9a**)[8] in 20 mL of tetrahydrofuran under nitrogen over a 20-min period and the stirring continued for 3 h. A 3 M sodium hydroxide solution, 32 mL, and 2.8 mL of 36% hydrogen peroxide were added successively, and the stirring mixture was warmed at 60 °C for 1 h. It then was diluted with 100 mL of water and extracted with ether. The extract was washed with water, dried, and evaporated. Chromatography of the residue and elution with 20:1 benzene–ethyl acetate led to 250 mg of starting diene **9a** and 2.10 g of amorphous alcohol **9b**: ^{1}H NMR δ 0.72, 0.88, 0.88, 0.95 (s, 3 each, methyls), 2.05 (s, 3, Ac Me), 3.68 (t, 2, J = 8 Hz, OCH_2), 4.40 (m, 1, OCH), 5.28 (m, 1, H-7).

Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41. Found: C, 75.86; H, 10.31.

3β-Acetoxy-13α-devinyl-13α-(carboxymethyl)isopimaradiene (9c). A solution of 10.0 mmol of Jones reagent (prepared from a solution of 70 g of chromium trioxide in 500 mL of water and 61 mL of concentrated sulfuric acid) was added slowly to a stirring solution of 2.10 g of alcohol **9b** in 100 mL of acetone at 0 °C, and the stirring was continued for 0.5 h. The excess of oxidizing agent was decomposed with a 5% sodium bisulfite solution. Water, 200 mL, was added and the mixture extracted with ether. The extract was washed with water, dried, and evaporated. Chromatography of the residue and elution with 100:1 chloroform–methanol yielded 1.80 g of semisolid acid **9c**: ^{1}H NMR δ 0.90, 0.90, 0.93, 0.98 (s, 3 each, methyls), 2.05 (s, 3, Ac Me), 2.22 (s, 2, $COCH_2$), 4.50 (m, 1, OCH), 5.30 (m, 1, H-7).

Anal. Calcd for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 72.96; H, 9.41.

3β-Acetoxy-13α-devinyl-13α-[β-(methoxycarbonyl)ethyl]isopimaradiene (9d). A solution of 1.80 g of acid **9c** in 10 mL of oxalyl chloride was stirred at room temperature under nitrogen for 2 h, and then the excess reagent was removed by vacuum distillation. A solution of the residue in 60 mL of dry ether was added over a 1-h period to a stirring solution of 10 mmol of diazomethane in 100 mL of anhydrous ether, containing 6 mL of triethylamine, at 0 °C under nitrogen, and the stirring was continued at room temperature for 2 h. The mixture was filtered and the filtrate evaporated under vacuum. Chromatography of the residue, 1.7 g, over neutral alumina (activity 4) and elution with 10:1 benzene–ethyl acetate yielded 1.60 g of semisolid diazo ketone: IR 2100 (C=N_2, s), 1725 (C=O, s), 1636 (COCN_2, s) cm^{-1}; ^{1}H NMR δ 0.88, 0.90, 0.90, 1.00 (s, 3 each, methyls), 2.06 (s, 3, Ac Me), 2.18 (s, 2, $COCH_2$), 4.40 (m, 1, OCH), 5.20 (s, 1, CHN_2), 5.30 (m, 1, H-7).

Silver oxide, 1.2 g, was added in portions to a stirring solution of 1.50 g of diazo ketone in 100 mL of anhydrous methanol at 60 °C, and the stirring was continued at this temperature for 2 h. The mixture was filtered and the filtrate evaporated under vacuum. The organic residue, 1.5 g, was chromatographed. Elution with 20:1 benzene–ethyl acetate gave 1.20 g of ester **9d**: ^{1}H NMR δ 0.73, 0.88, 0.88, 0.96 (s, 3 each, methyls), 2.04 (s, 3, Ac Me), 3.60 (s, 3, OMe), 4.50 (m, 1, OCH), 5.30 (m, 1, H-7).

Anal. Calcd for $C_{24}H_{38}O_4$: C, 73.80; H, 9.81. Found: C, 73.85; H, 9.77.

3β-Acetoxy-13α-devinyl-13α-[β-(methoxycarbonyl)ethyl]-7α-hydroxysandaracopimaradiene (10). Oxygen was bubbled slowly through a solution of 1.20 g of ester **9d** and 100 mg of eosine in 200 mL of ethanol, while the solution was being irradiated by a 250-W tungsten lamp. After 20 h the solution was poured into a solution of 1.0 g of sodium iodide in 20 mL of ethanol, and the mixture was kept at room temperature for 0.5 h. It then was concentrated under vacuum to a tenth of its volume and poured into 100 mL of water. It was extracted with 300 mL of chloroform, and the extract was washed with water, dried, and evaporated. Chromatography of the residue, 1.0 g, and elution with 6:1 benzene–ethyl acetate produced 800 mg of semisolid hydroxy ester **10**: ^{1}H NMR δ 0.78, 0.90, 0.90, 0.93 (s, 3 each, methyls), 2.05 (s, 3, Ac Me), 3.60 (s, 3, OMe), 4.05 (m, 1, C-7 OCH), 4.45 (m, 1, OCH), 5.31 (br. s, 1, H-14).

Anal. Calcd for $C_{24}H_{38}O_5$: C, 70.90; H, 9.42. Found: C, 70.85; H, 9.46.

3β-Acetoxy-6,7-dehydro-13α-devinyl-13α-[β-(methoxycarbonyl)ethyl]sandaracopimaradiene (11). Alcohol **10**, 800 mg, was dehydrated by the procedure of the preparation of triene **3** (vide supra). Chromatography of the residue and elution with 20:1 benzene–ethyl acetate afforded 480 mg of semisolid diene **11**: ^{1}H NMR δ 0.70, 0.91, 0.93, 0.98 (s, 3 each, methyls), 2.03 (s, 3, Ac Me), 3.60 (s, 3, OMe), 4.50 (m, 1, OCH), 5.18 (br. s, 1, H-14), 5.55 (dd, 1, J = 9, 1 Hz, H-7), 5.95 (dd, 1, J = 9, 4 Hz, H-6).

Anal. Calcd for $C_{24}H_{36}O_4$: C, 74.19; H, 9.34. Found: C, 74.23; H, 9.26.

Alcohols 12a and 12b. Ester **11**, 350 mg, was reduced by the procedure of the preparation of alcohols **4a** (vide supra). Chromatography of the residue, 240 mg, and elution with 20:1 benzene–ethyl acetate gave 60 mg of colorless, semisolid hydroxy acetate **12b**: ^{1}H NMR δ 0.86, 0.90, 0.97, 0.97 (s, 3 each, methyls), 2.00 (s, 3, Ac Me), 3.98 (m, 1, H-15), 4.45 (m, 1, OCH), 5.45 (m, 1, H-7).

Anal. Calcd for $C_{23}H_{36}O_3$: C, 76.62; H, 10.07. Found: C, 76.56; H, 10.12.

Further elution with 9:1 benzene–ethyl acetate yielded 80 mg of colorless, semisolid diol **12a**: ^{1}H NMR δ 0.82, 0.90, 0.98, 1.00, (s, 3 each, methyls), 3.20 (m, 1, OCH), 3.95 (m, 1, H-15), 5.45 (m, 1, H-7); ^{13}C NMR δ 37.8 (C-1), 27.3 (C-2), 69.1 (C-3), 40.0 (C-4), 49.7 (C-5), 23.3 (C-6), 123.2 (C-7), 135.9 (C-8), 48.9 (C-9), 35.1 (C-10), 20.9 (C-11), 34.8 (C-12), 38.5 (C-13), 63.4 (C-14), 75.6 (C-15), 37.9 (C-16), 30.7 (C-17), 28.1 (4α-Me), 15.4 (4β-Me), 14.4 (10β-Me), 25.9 (13β-Me). (C-1 and C-16 signals may be reversed.)

Anal. Calcd for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76. Found: C, 79.24; H, 10.70.

Keto Ester 12c. A solution of 30 mg of hydroxy ester **12b** in 3 mL of methylene chloride was added dropwise over a 15-min period to a suspension of 100 mg of Collins reagent in 5 mL of methylene chloride, and the mixture was stirred at room temperature for 15 min. It was filtered and the filtrate washed successively with 10% acetic acid solution, saturated sodium bicarbonate solution, and water. The organic solution was dried and evaporated under vacuum. Chromatography of the residue and elution with benzene gave 20 mg of colorless, semisolid ketone **12c**: IR 1700 (C=O, s), 1710 (C=O, s) cm^{-1}; ^{1}H NMR δ 0.84, 0.90, 0.97, 1.11 (s, 3 each, methyls), 2.00 (s, 3, Ac Me), 2.30 (s, 1, H-14), 4.45 (m, 1, OCH), 5.35 (m, 1, H-7); ^{13}C NMR δ 37.4 (C-1), 25.0 (C-2), 80.9 (C-3), 39.3 (C-4), 49.7 (C-5), 23.1 (C-6), 126.9 (C-7), 131.0 (C-8), 49.2 (C-9), 35.0 (C-10), 20.0 (C-11), 34.9 (C-12), 37.0 (C-13), 65.2 (C-14), 34.4 (C-16), 32.6 (C-17), 28.1 (4α-Me), 16.7 (4β-Me), 14.6 (10β-Me), 23.8 (13β-Me), 21.2 (Ac Me), 170.8 (Ac CO).

Anal. Calcd for $C_{23}H_{34}O_3$: C, 77.05; H, 9.56. Found: C, 77.16; H, 9.52.

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