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Potential Intermediates to Vitamin D_3 and Steroids: Enantioselective Syntheses of (20*R*)- and (20*S*)-De-AB-cholesta-8(14),22-dien-9-one from (*S*)- and (*R*)-2,3-*O*-Isopropylideneglyceraldehyde

Toshio SUZUKI,* Etsuko SATO and Katsuo UNNO

Department of Pharmaceutical Science, Akita University Hospital, Hondo 1-1-1, Akita 010, Japan.

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Enantioselective syntheses of both (20*R*)- and (20*S*)-de-AB-cholesta-8(14),22-dien-9-one (22 and 23), which are potential intermediates leading to vitamin D_3, steroids and their analogues, have been developed. The (3*R*)-methylcyclopentanone 12 was obtained through a known procedure starting with (*S*)-2,3-*O*-isopropylideneglyceraldehyde (8) or through inversion of the C_6 position in compound 5 using the Mitsunobu reaction followed by orthoester Claisen rearrangement. The construction of the *trans*-angularly methylated CD ring was accomplished through stereo- and regioselective Michael addition of the lithium enolate of 12 to α-silylated vinyl ketone, followed by intramolecular aldol condensation.

Keywords enantioselective synthesis; orthoester Claisen rearrangement; vitamin D_3; (*S*)-2,3-*O*-isopropylideneglyceraldehyde; *trans*-angularly methylated CD ring

The discovery of biologically important steroids possessing a modified side chain, such as ecdysone,[1] brassinolide,[2] and metabolities of vitamin D_3,[3] and the recent finding of a cell-differentiating effect of 1,25-dihydroxyvitamin D_3[4] and its analogues[5] have raised interest in the development of effective synthetic methods for steroids and related compounds. The enantioselective construction of the CD ring containing a requisite functional group at C_{17} (steroidal numbering)[6] which could be transformed into various types of side chain, would be useful in this regard.

Recently, we have reported the enantioselective synthesis of *trans*-octahydro-1,6-dioxoinden-4-ylpropionic acid,[7] a promising precursor of 11-keto steroids, from (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**1**).[8] Compound **1** and its enantiomer **8**[9] have now been converted to (20*R*)- and (20*S*)-de-AB-cholesta-8(14),22-dien-9-one (**22** and **23**),[10,11] synthetic precursors for metabolites of vitamin D, related compounds, and (20*S*)-sterols,[12] some of which possess interesting biologically activities.[13]

We present herein a full account of the experimental details of the synthetic procedure for optically active **22** and **23** from **1** and **8**.

The key intermediate **12**, possessing both the requisite stereochemistry and functional group for further elaboration of the side chain at C_{17}, can be accessed from **8**[14] through tandem orthoester Claisen rearrangement[14] followed by Dieckmann condensation *via* the (6*R*)-monoprotected allyl alcohol **11**, which could be also formed by the inversion of the C_6 position of the known compound **5**[7] obtained from **1**. A stereo- and regioselective Michael addition of the (3*S*)-methylcyclopentanone **12** to methyl vinyl ketone builds up the CD ring **16** possessing both the requisite functional group and stereochemistry at C_{17}. Introduction of the isobutyl group into the corresponding aldehyde **17** derived from **16**, followed by the combination of Claisen rearrangement and decarbonylation would provide the desired compounds **22** and **23**.

The key intermediate **12** was synthesized in 8 steps in 39% overall yield from **8**[9] prepared from L-ascorbic acid *via* compounds **9** and **11**, according to the procedure described in the previous paper.[7]

Next we examined a transformation of the known monoprotected allyl alcohol **5** derived from **1**[8] to the above key intermediate **11**. Solvolysis of the epoxide **6** prepared by selective tosylation of the primary alcohol in **2** gave a complex mixture. The only detectable compound was the acetate **4**, which on mild hydrolysis provided the starting diol **2**. However, the Mitsunobu reaction[15] of **5** proceeded smoothly to afford the desired compound **11** in 42.7% yield after hydrolysis of the corresponding benzoate **10**.

The formation of the *trans*-angularly methylated CD ring was achieved through stereo- and regioselective Michael addition and subsequent intramolecular aldol condensation. Michael addition of the lithium enolate generated from the silyl enol ether **13**, which was produced by reaction of **12** with hexamethyldisilazane and trimethylsilyl iodide[16] in quantitative yield, to α-silylated vinyl ketone[17] provided the diketone **15** as a sole product in 76.7% overall yield through compound **14**, whose trimethyl silyl group was removed during purification by silica gel column chromatography. Interestingly, neither a regio- nor a stereoisomer of the diketone **15** could be detected in this reaction. Base treatment[18] of **15** with 0.5 M KOH in 90% ethanol at 80°C resulted in cyclization and simultaneous deprotection of the *tert*-butyldimethylsilyl group to give the desired enone **16** in 93.3% yield.

Introduction of the methyl group at C_{20} (steroidal numbering) and further elaboration of the side chain were carried out in the following way. Grignard reaction of the aldehyde **17**, obtained in 88.8% yield by Swern oxidation[19] of **16**, with isobutylmagnesium chloride afforded the allyl alcohol **18** as an inseparable mixture of diastereoisomers at C_{22} (steroidal numbering) in 81.4% yield. Treatment of **18** with ethyl vinyl ether[9,20] containing mercuric acetate, followed by Claisen rearrangement of the resultant compound **19** provided the separable aldehydes **20** and **21** in 17.7 and 22.1% yields, respectively, along with the starting material **18** (13.6%). Decarbonylation[9,21] of **20** with tris(triphenylphosphine)rhodium chloride in refluxing benzene produced **22** in 50.1% yield. Similar treatment of the C_{20} epimer **21** gave **23** in 88.8%

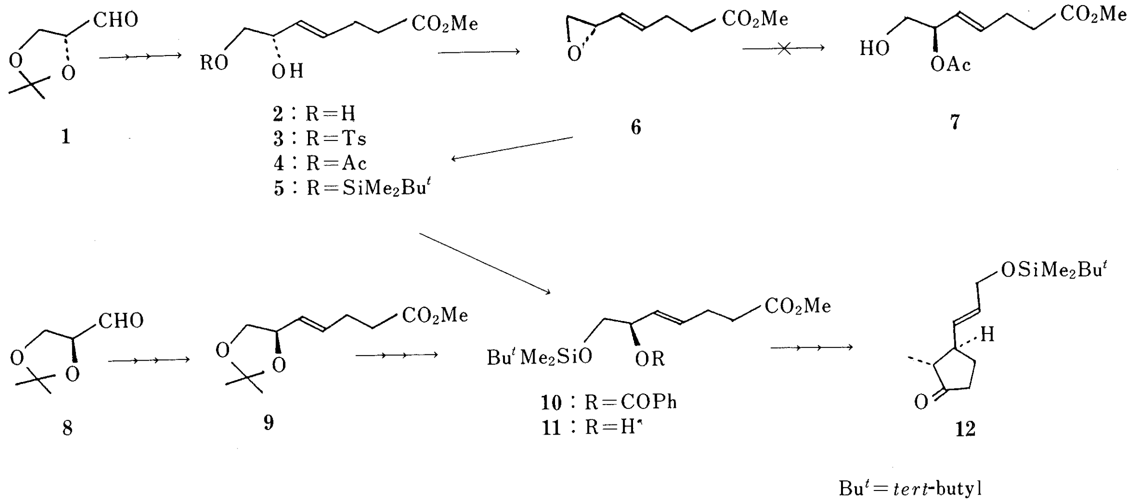

Chart 1

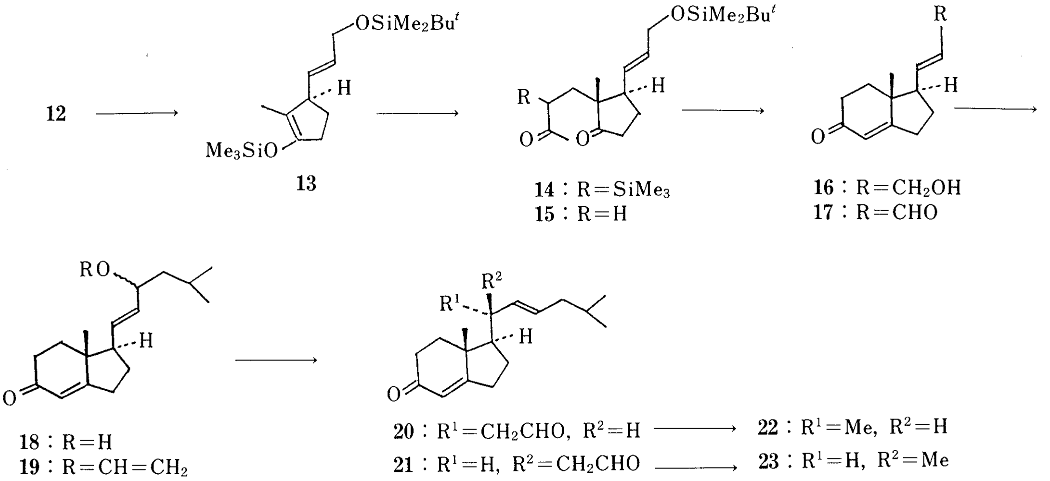

Chart 2

yield. Both products (**22** and **23**) had IR and ^{1}H-NMR spectra in accordance with published data.$^{10)}$

Experimental

Optical rotation was measured with a JASCO-DIP-4 automatic polarimeter. IR spectra were recorded on a JASCO IR-810 spectrophotometer. ^{1}H-NMR spectra were taken from solutions in deuteriochloroform with tetramethylsilane as internal standard on a JEOL JNM-PMX-60 or JNM-GX 400 instrument. MS spectra were obtained with a JEOL JMS-01-SG-2 spectrometer.

(2*R*,3*R*)-[3′-(*tert*-Butyldimethylsiloxy)prop-1′(*E*)-enyl]-2-methylcyclopentanone (12) The methylcyclopentanone **12** $[\alpha]_D^{27}$ $-46.6°$ ($c=1.52$ in $CHCl_3$) was obtained in 39% overall yield *via* **9** $[\alpha]_D^{20}$ $-25.8°$ ($c=0.72$ in $CHCl_3$), **11** $[\alpha]_D^{27}$ $-10.5°$ ($c=0.42$ in $CHCl_3$) and **12** $[\alpha]_D^{27}$ $-46.6°$ ($c=1.52$ in $CHCl_3$) from **8** using the same procedures as those described in the previous paper.$^{7)}$ IR, NMR, and MS spectra and TLC behavior of each compound were identical with those of the corresponding enantiomer.$^{7)}$

Examination of Inversion of the C_6 Position in the Diol 2 *via* the Epoxide 6 *p*-Toluenesulfonyl chloride (328 mg, 1.73 mmol) was added portionwise to a stirred solution of **2** (200 mg, 1.15 mmol) in dry pyridine (16 ml) at −10 °C. The mixture was stirred for 17 h at −0 °C to room temperature, and the reaction was quenched by addition of water. The solvent was removed under reduced pressure and the residue was extracted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and then evaporated to leave a residue, which was chromatographed on silica gel. Elution with hexane–ethyl acetate (65 : 35, v/v) gave **3** (277 mg, 73.6%, 87.6% based on recovered starting material) as a syrup. $[\alpha]_D^{25}$ +14.0° ($c=1.37$ in $CHCl_3$). IR ($CHCl_3$): 3600—3300 (OH), 1733 (C=O), 1362, 1176 (SO_2) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.32 (3H, s, Me), 3.60 (3H, s, Me), 5.33 (1H, dd, $J=16$, 5 Hz, 5-H), 5.55—6.07 (1H, m, 4-H), 7.30 (2H, each d, $J=8$ Hz, Ph-H), 7.77 (2H, each d, $J=8$ Hz, *ortho* Ph-H). MS *m*/*z*: 327 (M^+-1), and starting **2** (32 mg).

Potassium carbonate (50 mg, 0.362 mmol) was added to **3** (190 mg, 0.579 mmol) in methanol (2.5 ml) and the mixture was stirred for 24 h at room temperature. The solvent was evaporated to leave a residue, which was extracted with diethyl ether. The extract was washed successively with saturated aqueous sodium hydrogen carbonate and brine, then dried ($MgSO_4$). Evaporation of the solvent left a residue, which was chromatographed on silica gel with hexane–ethyl acetate (4 : 1, v/v) as the eluent to give **6** (74.2 mg, 82.1%) as a syrup. $[\alpha]_D^{25}$ +2° ($c=0.10$, $CHCl_3$). IR ($CHCl_3$): 1733 (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.60 (1H, dd, $J=6$, 2 Hz, 7-H), 2.90 (1H, dd, $J=6$, 4 Hz, 7-H), 3.27 (1H, ddd, $J=8$, 4, 2 Hz, 6-H), 3.63 (3H, s, Me), 5.17 (1H, dd, $J=14$, 8 Hz, 5-H), 5.63—6.30 (1H, m, 4-H). (Found: M^+, 156.0788. $C_8H_{12}O_3$ requires M^+, 156.0789).

Acetic acid (0.35 ml, 6.19 mmol) was added to a stirred solution of **6** (96.5 mg, 0.619 mmol) in dietyl ether at 0 °C and the mixture was stirred for 1 h at 0 °C, then extracted with diethyl ether. The extract was washed successively with saturated aqueous sodium hydrogen carbonate and brine, then dried ($MgSO_4$). Evaporation of the solvent left a residue, which was chromatgraphed on silica gel with hexane–ethyl acetate (1 : 1, v/v) as the eluent to give **4** (55.7 mg, 41.6%) as a syrup. $[\alpha]_D^{25}$ 4.4° ($c=0.41$, $CHCl_3$). IR ($CHCl_3$): 3606, 3650—3300 (OH), 1732 (C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$): 2.07 (3H, s, Me), 3.63 (3H, s, Me), 5.40 (1H, dd, $J=18$, 6 Hz, 5-H), 5.10—6.10 (1H, m, 4-H). MS *m*/*z*: 185 (M^+-31).

Potassium carbonate (3.3 mg, 0.024 mmol) was added to **4** (51.9 mg, 0.24 mmol) in methanol (1 ml) and the mixture was stirred for 13 h at room temperature. The solvent was evaporated to leave a residue, which was extracted with ethyl acetate. The extract was washed with brine, dried ($MgSO_4$), and evaporated to leave a residue, which was chromatographed on silica gel with hexane–ethyl acetate (1 : 1, v/v) as the eluent to give **2** (25.6 mg, 61.2%) as a syrup, whose TLC behavior, optical rotation, and IR and NMR spectra were identical with those of an authentic sample.

Transformation of the (6*R*)-Monoprotected Allyl Alcohol (5) into the (6*S*)-Monoprotected Allyl Alcohol (11) Diethyl azodicarboxylate (3.40 g, 29.3 mmol) in dry tetrahydrofuran (THF) (5 ml) was added dropwise to a solution of triphenylphosphine (7.67 g, 29.3 mmol), **5** (5.62 g, 19.5 mmol) and benzoic acid (2.38 g, 19.5 mmol) in dry THF (35 ml) at 0 °C, and the mixture was stirred for 15 h at room temperature. The solvent was removed to leave a residue, which was triturated with hexane–ethyl acetate (1 : 1, v/v) to give a crystalline solid. This was removed by filtration and the filtrate was concentrated to leave a residue. The residue was extracted with diethyl ether and the extract was washed successively with saturated aqueous sodium hydrogen carbonate and brine, then dried ($MgSO_4$). Evaporation of the solvent left a residue, which was chromatographed on silica gel with hexane–ethyl acetate (95 : 5, v/v) as the eluent to give **10** (6.8 g) as a syrup.

Potassium carbonate (1.20 g, 8.65 mmol) was added to **10** (6.8 g, 17.3 mmol) in methanol (95 ml) and the mixture was stirred for 15 h at room temperature. The solvent was evaporated to leave a residue, which was extracted with diethyl ether. The organic layer was separated and washed successively with aqueous saturated sodium hydrogen carbonate and brine, dried ($MgSO_4$) and then evaporated to give a residue, which was chromatographed on silica gel with hexane–ethyl acetate (4 : 1, v/v) as the eluent to afford **11** (2.40 g, 42.7% overall yield from **5**) $[\alpha]_D^{25}$ $-10.5°$ ($c=1.01$ in $CHCl_3$) as a syrup. IR, NMR and MS spectra were identical with those of **5**.

(2*R*,3*R*)-3-[3′-(*tert*-Butyldimethylsiloxy)prop-1′(*E*)-enyl)-2-methyl-2-(3′-oxo-butyl)cyclopentanone (15) Hexamethyldisilazane (179 mg, 1.08 mmol) and trimethylsilyl iodide (179 mg, 0.897 mmol) were added to a stirred solution of **12** (80 mg, 0.299 mmol) in dichloromethane (1 ml) at −20°C under nitrogen, containing one piece of 4 Å molecular sieve. The mixture was stirred under nitrogen for 15 min at −20 °C, and for an additional 4 h at room temperature. After the reaction had gone to completion, the mixture was extracted with dry diethyl ether. The extract was washed with ice-cold saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and then concentrated. The residue was passed rapidly through a short silica gel column with 3 drops of triethylamine in hexane–ethyl acetate (9 : 1, v/v) as the eluent to give the pure silyl enol ether **13** (101 mg, quantitative yield) as a sole product.

A solution of methyllithium (1.4 M in Et_2O) (0.32 ml, 0.449 mmol) was added dropwise to a stirred solution of the above silyl enol ether **13** (101 mg, 0.299 mmol) in dry THF (0.5 ml) at −50 °C under nitrogen, and the mixture was stirred for 30 min at room temperature. To this lithium enolate was added a solution of 2-trimethylsilyl-1-buten-3-one (100 mg, 0.897 mmol) in dry THF (0.5 ml) at −78 °C over 5 min under nitrogen, and the mixture was stirred for 40 min at −78 °C. The reaction was then quenched by addition of saturated aqueous ammonium chloride, and the mixture was extracted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and then concentrated to give **14**, which was chromatographed on silica gel with hexane–ethyl acetate (4 : 1, v/v) as the eluent to provide **15** (69.6 mg, 76.7%) as a syrup. $[\alpha]_D^{21}$ $-22.9°$ ($c=0.37$ in $CHCl_3$). IR ($CHCl_3$): 1732, 1719 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$): 0.07 (6H, s, $SiMe_2$), 0.83 (3H, s, Me), 0.87 (9H, s, *tert*-Bu), 3.95—4.22 (2H, m, CH_2OSi), 5.38—5.67 (2H, m, CH=CH). (Found: *m/z*, 281.1573 (M^+-57). $C_{15}H_{24}O_3Si$ requires *m/z*, 281.1573 (M^+-57)), and further elution with the same solvent provided the starting material **12** (8.1 mg, 10.1%).

(1*R*,7a*R*)-1-(3′-Hydroxyprop-1′(*E*)-eny]-7a-methyl-5-oxo-2,3,6,7,7a-pentahydroindene (16) Compound **15** (46.8 mg, 0.138 mmol) was treated with 0.5% KOH in 90% ethanol (0.5 ml, 0.069 mmol). The mixture was heated at 80 °C for 2 h. After the reaction had gone to completion, the mixture was cooled to room temperature, and neutralized with 6 N HCl. The solvent was evaporated off to leave a residue, which was extracted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and then evaporated to leave a residue, which was chromatographed on silica gel. Elution with hexane–ethyl acetate (1 : 1, v/v) afforded **16** (26.6 mg, 93.3%) as a syrup. $[\alpha]_D^{21}$ $+41.3°$ ($c=0.18$ in $CHCl_3$). IR ($CHCl_3$): 3608, 3700—3200 (OH), 1656 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$, 400 MHz): 1.03 (3H, s, Me), 4.10—4.23 (2H, m, CH_2OH), 5.68 (1H, dd, $J=14.8$, 6.8 Hz, $CHC\underline{H}=CH$), 5.72—5.76 (1H, m, $CH=C\underline{H}CH_2$), 5.78 (1H, s, enone). (Found: M^+, 206.1299. $C_{13}H_{18}O_2$ requires M^+, 206.1305).

(1*R*,7a*R*)-1-(2′-Formyl-1′(*E*)-enyl)-7a-methyl-5-oxo-2,3,6,7,7a-pentahydroindene (17) Dimethyl sulfoxide (DMSO) (341 mg, 4.36 mmol) was added dropwise to a stirred solution of oxalyl chloride (277 mg, 2.18 mmol) in dichloromethane (2 ml) at −78 °C under nitrogen. The mixture was stirred for 3 min, a solution of **16** (225 mg, 109 mmol) in dichloromethane (2 ml) was added dropwise and the whole was stirred for 10 min at −78 °C, then triethylamine (882 mg, 8.72 mmol) was added all at once. The mixture was stirred for 15 min at room temperature. The reaction was quenched by addition of water and the mixture was extracted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated to leave a residue, which was chromatographed on silica gel with hexane–ethyl acetate (1 : 1, v/v) as the eluent to provide **17** (200 mg, 89.8%) as a syrup. $[\alpha]_D^{22}$ $+54.3°$ ($c=0.20$ in $CHCl_3$). IR ($CHCl_3$): 1689, 1667 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$): 1.08 (3H, s, CH_3), 5.72 (1H, s, enone), 6.08 (1H, dd, $J=16$, 7 Hz, $CH=C\underline{H}CHO$), 6.75 (1H, dd, $J=16$, 7 Hz, $C\underline{H}=CHCHO$), 9.43 (1H, d, $J=7$ Hz, $CH=CHC\underline{H}O$). (Found: M^+, 204.1152. $C_{13}H_{16}O_2$ requires M^+, 204.1153).

(1*R*,7a*R*)-1-[3′-Hydroxy-5′-methyl-1′(*E*)-hexenyl]-7a-methyl-5-oxo-2,3,6,7,7a-pentahydroindene (18) A solution of isobutylmagnesium chloride (2 M in Et_2O) (52 μl, 0.104 mmol) was added dropwise to a stirred solution of **17** (17.7 mg, 0.0868 mmol) in dichloromethane (0.4 ml) at −40 °C. The reaction mixture was stirred for 15 min at −40 °C and then quenched with saturated aqueous ammonium chloride. The mixture was diluted with diethyl ether. The extract was washed with brine, dried ($MgSO_4$), and evaporated to leave a residue, which was chromatographed on silica gel with hexane–ethyl acetate (6 : 5, v/v) as the eluent to give **18** (18.5 mg, 81.4%) as a syrup. $[\alpha]_D^{27}$ $+36.5°$ ($c=1.26$ in $CHCl_3$). IR ($CHCl_3$): 3600, 3550—3300 (OH), 1657 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$): 0.92 [6H, d, $J=6$ Hz, $C(CH_3)_2$], 1.00 (3H, s, Me), 3.93—4.35 (1H, m, $C\underline{H}OH$), 5.17—5.63 (2H, m, CH=CH), 5.69 (1H, s, enone). (Found: M^+, 262.1932. $C_{17}H_{26}O_2$ requires M^+, 262.1932).

(1*R*,7a*R*,1′*R*)-1-[1′-Formylmethyl-5′-methyl-2′(*E*)-hexenyl]-7a-methyl-5-oxo-2,3,6,7,7a-pentahydroindene (20) and (1*R*,7a*R*,1′*S*)-1-[1′-Formylmethyl-5′-methyl-2′(*E*)-hexenyl]-7a-methyl-5-oxo-2,3,6,7,7a-pentahydroindene (21) Compound **18** (48.9 mg, 0.187 mmol) was dissolved in ethyl vinyl ether (1.35 g, 18.7 mmol) containing mercuric acetate (47.7 mg, 0.150 mmol). The solution was heated at reflux under nitrogen for 17 h, cooled to room temperature, and then treated with glacial acetic acid (2 μl). After being stirred for another 2 h at room temperature, the reaction mixture was diluted with diethyl ether, washed with 5% potassium hydroxide, and then dried ($MgSO_4$). The solvent was evaporated to leave a residue, which was passed through a short alumina column using diethyl ether as the eluent. The solvent was removed to give a mixture of the labile vinyl ether **19** and the starting allyl alcohol **18**.

The resultant mixture was heated in collidine (0.5 ml) at 150 °C for 1 h. The solvent was removed *in vacuo* to leave a residue, which was chromatographed on silica gel with hexane–ethyl acetate (85 : 15, v/v) to provide **21** (11.9 mg, 22.1%) as a syrup. $[\alpha]_D^{25}$ $+92.4°$ ($c=0.12$ in $CHCl_3$). IR ($CHCl_3$): 1722, 1658 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$): 0.87 (6H, d, $J=6$ Hz, $C(CH_3)_2$), 1.13 (3H, s, CH_3), 4.93—5.57 (2H, m, CH=CH), 5.70 (1H, s, enone), 9.57 (1H, t, $J=2$ Hz, CHO). (Found: M^+ 288.2088. $C_{19}H_{28}O_2$ requires M^+, 288.2088). Its epimer **20** (9.5 mg, 17.7%) as a syrup, $[\alpha]_D^{25}$ $+30.6°$ ($c=0.09$ in $CHCl_3$). IR ($CHCl_3$): 1722, 1658 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$): 0.87 [6H, d, $J=6$ Hz, $C(CH_3)_2$], 1.13 (3H, s, CH_3), 4.93—5.57 (2H, m, CH=CH), 5.70 (1H, s, enone), 9.63 (1H, t, $J=2$ Hz, CHO). (Found: M^+ 288.2088. $C_{19}H_{28}O_2$ requires M^+, 288.2088), and the starting allyl alcohol **18** (6.7 mg, 13.6%).

(20*R*)-De-AB-cholesta-8(14),22-dien-9-one (22) Compound **20** (9.5 mg, 0.041 mmol) was dissolved in benzene (0.3 ml) containing tris(triphenylphosphine)rhodium chloride (55.4 mg, 0.061 mmol) and the mixture was refluxed for 1.5 h with stirring under nitrogen. After the reaction had gone to completion, the mixture was diluted with diethyl ether and insoluble material was removed by filtration. The filtrate was dried ($MgSO_4$) and then evaporated to leave a residue, which was purified by preparative TLC on silica gel developed with hexane–ethyl acetate (4 : 1, v/v) to afford **22** (4.3 mg, 50.1%) as a syrup, *Rf*=0.45 (hexane : ethyl acetate= 4 : 1, v/v). $[\alpha]_D^{25}$ $+28.2°$ ($c=0.04$ in $CHCl_3$). IR ($CHCl_3$): 1653 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$, 400 MHz): 0.88 [6H, d, $J=6.6$ Hz, $C(CH_3)_2$], 1.06 (3H, d, $J=6.6$ Hz, CH_3), 1.11 (3H, s, CH_3), 5.25 (1H, dd, $J=15.4$, 8.3 Hz, $CC\underline{H}=CH$), 5.33—5.41 (1H, m, $CCH=C\underline{H}$), 5.73 (1H, s, enone). (Found: M^+, 260.2148, $C_{18}H_{28}O$ requires M^+, 260.2139).

(20*S*)-De-AB-isocholesta-8(14),22-dien-9-one (23) Compound **21** (7.3 mg, 0.025 mmol) was also converted into the (20*S*)-isomer **23** (5.9 mg, 88.8%) as a syrup by using the same procedure as described above,

$Rf=0.48$ (hexane : ethyl acetate = 4 : 1, v/v). $[\alpha]_D^{25}$ +74.3° ($c=0.06$ in $CHCl_3$). IR ($CHCl_3$): 1653 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$, 400 MHz): 0.88 (6H, d, $J=6.8$ Hz, $C(CH_3)_2$), 1.00 (3H, d, $J=6.8$ Hz, CH_3), 1.08 (3H, s, CH_3), 5.23 (1H, dd, $J=15.3$, 9.2 Hz, $CC\underline{H}=CH$), 5.35—5.42 (1H, m, $CCH=C\underline{H}$), 5.72 (1H, s, enone). (Found: M^+ 260.2139. $C_{18}H_{28}O$ requires M^+, 260.2139).

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