

Unless otherwise specified, ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 at 400 MHz on a Varian Inova-400 spectrometer or at 75 MHz on a Mercury-300 spectrometer, respectively. Chemical shifts are given in ppm relative to internal CHCl_3 (^1H , $\delta = 7.27$, ^{13}C , $\delta = 77.26$). Optical rotations were measured on a Rudolph Research Analytical Autopol® IV Polarimeter.

New compounds reported in this study are: III, S-III, S-V, S-XV, S-XVI, S-XXII, XXIII, S-XXIII, XXIV, XXVII.

Scheme 1:

(25R)-Cholest-5-ene-3 β ,16 β ,26-triol (VII)

^1H NMR: δ 0.87-0.90 (m, 6H), 0.96-1.00 (m, 6H), 1.04-1.20 (m, 3H), 1.30-1.57 (m, 12H), 1.61 (s, 3H), 1.76-1.88 (m, 3H), 1.92-2.05 (m, 2H), 2.17-2.33 (m, 3H), 3.40-3.56 (m, 3H), 4.34 (dt, 1H, $J=4.57, 4.39$), 5.32-5.36 (m, 1H);

^{13}C NMR: δ 13.24, 16.85, 18.37, 19.59, 20.88, 23.92, 29.85, 31.67, 31.81, 31.99, 33.52, 35.82, 36.15, 36.71, 36.82, 37.37, 40.03, 42.39, 42.46, 50.26, 54.67, 61.68, 68.65, 71.96, 72.66, 121.67, 141.07.

(25R)-3 β ,26-Bis(tert-butyltrimethylsilyloxy)cholest-5-en-16 β -ol (VIII)

^1H NMR: δ 0.02 (s, 6H), 0.04 (s, 6H), 0.76-1.21 (m, 38H), 1.21-1.64 (m, 10H), 1.65-1.9 (m, 3H), 1.9-2.08 (m, 2H), 2.10-2.31 (m, 3H), 3.3-3.51 (m, 3H), 4.28-4.37 (m, 1H), 5.27-5.314 (m, 1H);

^{13}C NMR: δ -5.11, -4.36, 13.22, 16.91, 18.41, 18.46, 18.58, 19.63, 20.88, 23.96, 26.15, 26.19, 29.95, 31.69, 32.04, 32.26, 33.81, 35.99, 36.50, 36.73, 36.79, 37.52, 40.08, 42.39, 42.99, 50.37, 54.74, 61.59, 68.69, 72.65, 72.79, 121.13, 141.83.

(25R)-3 β ,26-Bis(tert-butyltrimethylsilyloxy)cholest-5-en-16-one (IX)

^1H NMR: δ 0.016 (s, 6H), 0.045 (s, 6H), 0.72-0.92 (m, 24H), 0.92-0.98 (m, 3H), 0.98-1.14 (m, 6H), 1.14-1.46 (m, 6H), 1.46-1.85 (m, 12H), 1.86 (m, 1H), 2.02-2.12 (m, 1H), 2.12-2.32 (m, 3H), 3.28-3.53 (m, 3H), 5.26-5.32 (m, 1H);

^{13}C NMR: δ -5.12, -4.38, 13.88, 16.92, 18.46, 18.57, 18.88, 19.64, 20.72, 24.83, 26.13, 26.18, 30.95, 31.47, 32.03, 32.18, 33.54, 35.97, 36.13, 36.88, 37.28, 39.13, 39.16, 42.94, 43.19, 50.13, 51.15, 68.15, 68.71, 72.68, 120.67, 141.94, 218.96.

(25R)-Cholest-5-ene-3 β ,26-diol (X)

^1H NMR: δ 0.66 (s, 3H), 0.8-1.17 (m, 18H), 1.17-1.4 (m, 8H), 1.4-1.66 (m, 10H), 1.72-1.88 (m, 3H), 1.9-2.02 (m, 2H), 2.08-2.19 (m, 6H), 2.19-2.34 (m, 2H), 3.35-3.57 (m, 3H), 5.29-5.36 (m, 1H).

Scheme 2

(25R)-Cholest-4-ene-3-one-26-ol (XI)

^1H NMR: δ 0.68 (s, 3H), 0.85-0.92 (m, 6H), 0.94-1.18 (m, 10H), 1.19-1.74 (m, 12H), 1.75-1.90 (m, 2H), 1.95-2.05 (m, 2H), 2.20-2.45 (m, 4H), 3.35-3.52 (m, 2H), 5.69 (s, 1H) [olefin C-4];
 ^{13}C NMR: δ 12.12, 16.69, 17.54, 18.76, 21.87, 23.57, 24.34, 28.37, 32.20, 33.12, 33.68, 34.14, 35.76, 35.84, 35.96, 36.25, 38.77, 39.78, 42.55, 53.96, 56.03, 56.25, 68.64, 123.89, 172.00, 199.95.

(25R)-Cholest-4-ene-3-one-26-oic acid (Δ^4 -dafachronic acid, II)

$[\alpha]_D +8.5$ (c 0.2, CDCl_3);

^1H NMR: δ 0.69 (s, 3H), 0.89 (d, 3H, $J=6.4$ Hz), 0.94-1.20 (m, 12H), 1.30-1.74 (m, 12H), 1.75-1.89 (m, 2H), 1.93-2.07 (m, 2H), 2.20-2.51 (m, 6H), 5.71 (bs, 1H).
 ^{13}C NMR: δ 12.14, 16.95, 17.56, 18.75, 21.19, 23.80, 24.35, 28.36, 32.20, 33.15, 34.07, 34.13, 35.77, 35.84, 38.79, 39.51, 39.77, 42.57, 53.95, 56.02, 56.19, 123.91, 172.17, 182.94, 200.13.

(25R)-3 β ,26-Bis(tert-butyltrimethylsilyloxy)cholest-5-ene (XII)

^1H NMR: δ -0.010 (s, 6H), 0.026 (s, 6H), 0.667 (s, 3H), 0.79-1.67 (m, 48H), 1.75-1.85 (m, 3H), 1.90-2.06 (m, 2H), 2.14-2.34 (m, 2H), 3.33 (dd, 1H, $J=9.70$, 6.59 Hz), 3.42 (dd, 1H, $J=9.70$, 6.04 Hz), 3.46-3.57 (m, 1H), 5.31-5.37 (m, 1H);
 ^{13}C NMR: δ -5.10, -4.36, 12.07, 16.91, 18.49, 18.92, 19.66, 21.28, 23.57, 24.51, 26.17, 26.20, 28.48, 32.12, 32.16, 32.31, 33.80, 35.93, 35.96, 36.40, 36.80, 37.61, 40.03, 42.54, 43.04, 50.42, 56.36, 57.02, 68.77, 72.86, 121.40, 141.76.

(25R)-Cholest-5-ene-3 β -tert-butyltrimethylsilyloxy-26-ol (XIII)

^1H NMR: δ 0.045 (s, 6H), 0.658 (s, 3H), 0.8-1.5 (m, 38H), 1.57 (s, 14H), 1.67-1.90 (m, 3H), 1.9-2.08 (m, 2H), 2.08-2.36 (m, 2H), 3.32-3.58 (m, 2H), 5.25-5.33 (m, 1H).

(25R)-Cholest-5-ene-3 β -tert-butyltrimethylsilyloxy-26-al (XIV)

^1H NMR: δ -0.043 (s, 6H), 0.66 (s, 3H), 0.78-0.96 (m, 16H), 0.95-1.30 (m, 18H), 1.3-2.4 (m, 24H), 3.46 (qt, 1H, $J=4.9$ Hz), 5.26-5.35 (m, 1H), 9.60 (d, 1H, $J=2.1$ Hz).

(25R)-Cholest-5-ene-3 β -tert-butyltrimethylsilyloxy-26-oic acid (XV)

^1H NMR: δ 0.67 (s, 3H), 0.82-1.75 (m, 40H), 1.76-1.93 (m, 2H), 1.93-2.10 (m, 2H), 2.19-2.40 (m, 2H), 2.40-2.56 (m, 1H), 3.46-3.60 (m, 1H), 5.31-5.40 (m, 1H).

(25R)-Cholest-5-ene-3 β -ol-26-oic acid (XVI)

^1H NMR: δ 0.66 (s, 3H), 0.79-0.94 (m, 6H), 0.97-1.14 (m, 8H), 1.14-1.69 (m, 38H), 1.74-1.88 (m, 3H), 1.91-2.08 (m, 4H), 2.15-2.39 (m, 3H), 2.41-2.52 (m, 1H), 3.46-3.57 (m, 1H), 5.32-5.36 (m, 1H).

(25R)-Cholest-5-ene-3-one-26-oic acid (Δ^5 -dafachronic acid, III)

^1H NMR: δ 0.69 (s, 3H), 0.79-1.22 (m, 8H), 1.22-2.17 (m, 30H), 2.26-2.63 (m, 4H), 5.28-5.42 (m, 1H) [olefin C-6].

^{13}C NMR: δ 12.12, 16.98, 18.85, 19.40, 21.23, 21.56, 23.85, 24.48, 28.44, 32.02, 32.11, 34.12, 35.85, 35.93, 37.12, 37.88, 39.50, 39.85, 42.60, 48.58, 49.34, 56.24, 56.79, 123.13 [olefin C-6], 138.75 [olefin, C-5], 182.72, 210.79.

Scheme 3

(25R)-3 β ,26-Bisacetoxy-cholest-5-ene (XVII)

^1H NMR: δ 0.66 (s, 3H), 0.86-1.4 (m, 24H), 1.4-1.66 (m, 9H), 1.7-1.9 (m, 4H), 1.9-2.0 (m, 2H), 2.02 (s, 3H), 2.04 (s, 3H), 2.24-2.36 (m, 2H), 3.83 (dd, 1H, $J=10.6, 6.9$ Hz), 3.93 (dd, 1H, $J=10.6, 6.0$ Hz), 4.52-4.65 (m, 1H), 5.36 (d, $J=4.7$ Hz);

^{13}C NMR (75 Hz, CDCl_3): δ 12.07, 17.00, 18.88, 19.53, 21.22, 21.66, 23.44, 24.48, 27.97, 28.46, 32.06, 32.09, 32.70, 33.95, 35.91, 36.24, 36.79, 37.19, 38.33, 39.92, 42.52, 50.21, 56.28, 56.87, 69.83, 74.18, 122.84, 139.85, 170.76, 171.54.

(25R)-3 β ,26-Bisacetoxy-cholest-5-ene-7-one (XVIII)

^1H NMR: δ 0.68 (s, 3H), 0.87-0.98 (m, 6H), 0.98-1.45 (m, 16H), 1.47-1.62 (m, 6H), 1.62-1.84 (m, 2H), 1.84-2.10 (m, 10H), 2.16-2.29 (m, 1H), 2.34-2.61 (m, 3H), 3.84 (dd, 1H, $J=10.73, 6.8$ Hz), 3.94 (dd, 1H, $J=10.73, 4.68$ Hz), 4.66-4.77 (m, 1H), 5.71 (d, 1H, $J=1.8$ Hz);

^{13}C NMR: δ 11.60, 11.97, 16.69, 18.64, 20.86, 21.22, 21.68, 23.09, 24.85, 27.00, 28.35, 32.32, 33.56, 33.73, 35.47, 35.72, 35.82, 35.87, 38.61, 42.39, 45.73, 46.33, 48.80, 49.76, 54.83, 54.89, 69.37, 72.61, 170.20, 170.99, 211.12.

(25R)-3 β ,26-Bisacetoxy-cholest-7-one (XIX)

^1H NMR: δ 0.63 (s, 3H), 0.86-0.93 (m, 6H), 1.06-1.1 (m, 6H), 1.14-1.42 (m, 8H), 1.42-1.72 (m, 8H), 1.68-1.82 (m, 3H), 1.82-1.98 (m, 3H), 1.98-2.08 (m, 6H), 2.12-2.24 (m, 1H), 2.31 (t, 2H, $J=11.7$ Hz), 3.82 (dd, 1H, $J=10.74, 6.8$ Hz), 3.91 (dd, 1H, $J=10.74, 6.05$ Hz), 4.65 (qt, 1H, $J=5.27$ Hz);

^{13}C NMR (300 MHz, CDCl_3): δ 11.93, 12.28, 16.96, 18.94, 21.22, 21.58, 21.99, 23.42, 25.19, 27.31, 28.65, 32.66, 33.88, 34.04, 35.81, 36.03, 36.17, 36.19, 38.89, 42.73, 46.09, 46.71, 49.07, 50.17, 55.19, 69.81, 73.00, 170.74, 171.57, 211.84.

(25R)-3 β ,26-Bisacetoxy-cholest-7 α -ol (XX)

^1H NMR: δ 0.54-0.66 (m, 3H), 0.69-0.94 (m, 10H), 0.94-1.18 (m, 8H), 1.18-1.59 (m, 20H), 1.59-1.89 (m, 6H), 1.89-2.80 (m, 6H), 3.70-3.98 (m, 3H), 4.58-4.76 (m, 1H);

^{13}C NMR: δ 11.30, 11.99, 16.92, 18.76, 21.11, 21.56, 23.35, 23.75, 27.55, 28.41, 32.60, 33.75, 33.84, 35.66, 35.85, 36.13, 36.56, 36.63, 36.99, 39.61, 39.70, 42.73, 45.77, 50.60, 56.24, 67.75, 69.74, 73.79, 170.73, 171.43.

(25R)-3 β ,26-Bisacetoxy-cholest-7-ene (XXI)

^1H NMR: δ 0.52 (s, 1H), 0.8 (s, 3H), 0.9 (d, 6H, $J=6.8$ Hz), 0.98-1.52 (m, 18H), 1.56 (s, 4H), 1.62-1.96 (m, 8H), 2.03 (d, 6H, $J=11.9$ Hz), 3.83 (dd, 1H, $J=10.54, 7.03$ Hz), 3.93 (dd, 1H, $J=10.73, 6.05$ Hz), 4.60-4.76 (m, 1H), 5.10-5.17 (m, 1H) [olefin, C-7];

^{13}C NMR: δ 11.96, 13.05, 14.32, 16.90, 18.90, 21.09, 21.56, 21.58, 23.04, 23.42, 27.60, 28.08, 29.64, 32.60, 33.83, 33.91, 34.29, 36.08, 36.22, 36.94, 39.60, 40.14, 43.46, 49.35, 55.08, 56.19, 60.48, 69.69, 73.54, 117.45, 139.56, 170.74, 171.37.

(25R)-Cholest-7-ene-3 β ,26-diol (XXII)

^1H NMR: δ 0.46-0.7 (m, 3H), 0.74-0.86 (m, 4H), 0.86-0.96 (m, 6H), 0.96-1.17 (m, 4H), 1.17-1.51 (m, 16H), 1.51-1.67 (m, 8H), 1.67-2.08 (m, 8H), 2.12-2.40 (m, 1H), 3.34-3.66 (m, 3H), 5.1-5.2 (m, 1H);

^{13}C NMR: δ 12.08, 13.27, 16.73, 19.02, 21.77, 23.17, 23.71, 28.20, 29.86, 31.68, 33.74, 34.42, 36.03, 36.31, 36.35, 37.35, 38.19, 39.77, 40.45, 43.61, 49.64, 55.25, 56.33, 68.75, 71.27, 117.68, 139.80.

(25R)-Cholest-7-ene-3-one-26-al (XXIII)

^1H NMR: δ 0.54(s, 3H), 0.914 (d, 4H, $J=6.4$ Hz), 1.00 (s, 3H), 1.08 (d, 4H, $J=7.0$ Hz), 1.14-1.50 (m, 16H), 1.54 (s, 12H), 1.57-1.95 (m, 10H), 1.98-2.16 (m, 3H), 2.16-2.47 (m, 6H), 5.14-5.19 (m, 1H), 9.61 (d, 1H, $J=1.9$ Hz);

^{13}C NMR: δ 12.12, 12.70, 13.52, 18.99, 21.90, 23.14, 23.69, 28.17, 30.26, 31.10, 34.60, 36.01, 36.25, 38.34, 38.97, 39.61, 43.06, 43.58, 44.46, 46.60, 49.02, 55.12, 56.16, 117.27, 139.67, 205.75, 212.41.

(25R)-Cholest-7-ene-3-one-26-oic acid (Δ^7 -dafachronic acid, I)

$[\alpha]_D^{+11.0}$ (c 2.0, CDCl_3) cf. Lit. $+18.4$ (c 2.0, CDCl_3) (1).

^1H NMR: δ 0.55 (s, 3H), 0.82-0.96 (m, 6H), 1.00 (s, 3H), 1.12-1.36 (m, 16H), 1.36-1.94 (m, 28H), 1.94-2.17 (m, 3H), 2.17-2.33 (m, 3H), 2.33-2.55 (m, 3H), 5.13-5.20 (m, 1H) [olefin, C-7];

^{13}C NMR: δ 12.11, 12.68, 16.97, 18.97, 21.89, 23.14, 23.92, 28.14, 29.92, 30.26, 34.10, 34.59, 35.86, 36.25, 38.33, 38.97, 39.61, 43.06, 43.57, 44.45, 49.03, 55.11, 56.24, 117.23, 139.69, 212.37.

Scheme 4

Δ^7 Series

(25R,S)-Cholest-7-ene-3-one-26-al (R/S-XXIII)

^1H NMR: δ 0.55 (s, 3H), 0.40-0.80 (m, 4H), 1.00 (s, 3H), 1.08 (m, 4H), 1.14-1.54 (m, 16H), 1.5 (s, 6H), 1.59-1.96 (m, 12H), 1.97-2.17 (m, 4H), 2.18-2.49 (m, 8H), 5.14-5.19 (m, 1H), 9.59-9.62 (m, 1H) [aldehyde, pseudo-triplet];

^{13}C NMR: δ 12.07, 12.64, 13.47, 13.64, 18.94, 18.96, 21.85, 23.09, 23.63, 23.69, 28.12, 30.21, 31.04, 31.21, 34.55, 35.96, 36.03, 36.20, 36.23, 38.30, 38.92, 39.56, 43.01, 43.53, 44.41, 46.55, 46.59, 48.97, 55.06, 56.11, 117.22, 139.63, 205.68, 212.29.

(25R,S)-Cholest-7-ene-3,26-diol (R/S-XXII)

¹H NMR: δ 0.52 (s, 3H), 0.73-0.85 (m, 4H), 0.86-0.97 (m, 7H), 0.98-1.14 (m, 4H), 1.14-1.49 (m, 16H), 1.49-1.67 (m, 10H), 1.67-1.93 (m, 6H), 1.95-2.06 (m, 1H), 3.36-3.67 (m, 3H), 5.10-5.20 (m, 1H);

¹³C NMR: δ 12.03, 13.24, 16.69, 16.92, 18.97, 21.70, 23.12, 23.66, 23.70, 28.15, 29.81, 31.59, 33.69, 33.82, 34.35, 35.96, 36.26, 36.31, 36.36, 37.30, 38.10, 39.72, 40.39, 43.54, 49.58, 55.19, 56.25, 56.27, 68.48, 68.67, 71.21, 117.63, 139.75.

(25S)-Cholest-7-ene-26-acetoxy-3-ol (XXIV)

¹H NMR: δ 0.51 (s, 3H), 0.78 (s, 3H), 0.89-0.94 (m, 6H), 0.98-1.56 (m, 18H), 0.73-0.85 (m, 4H), 0.86-0.97 (m, 7H), 0.98-1.14 (m, 4H), 1.14-1.49 (m, 16H), 1.57 (s, 5H), 1.68-1.94 (m, 8H), 2.04 (s, 3H), 3.53-3.66 (m, 1H), 3.82 (dd, 1H, J=10.55, 6.83 Hz), 3.94 (dd, 1H, J=10.73, 5.85 Hz), 5.12-5.20 (m, 1H);

¹³C NMR: δ 12.07, 13.28, 17.26, 19.07, 21.25, 21.76, 23.17, 23.58, 28.16, 29.86, 31.67, 32.77, 34.09, 34.41, 36.30, 36.39, 37.35, 38.18, 29.76, 40.44, 43.60, 49.63, 55.23, 56.26, 69.72, 71.27, 117.69, 139.79, 171.64.

(25S)-Cholest-7-ene-3,26-diol (S-XXII)

¹H NMR: δ 0.52 (s, 3H), 0.78 (s, 3H), 0.89-0.94 (m, 6H), 0.98-1.9 (m, 36H), 1.97-2.04 (m, 1H), 3.35-3.63 (m, 3H), 5.11-5.17 (m, 1H);

¹³C NMR: δ 12.05, 13.26, 16.93, 19.06, 21.73, 23.15, 23.72, 28.16, 29.83, 31.64, 33.84, 34.38, 36.02, 36.39, 37.32, 38.15, 39.74, 40.42, 43.57, 49.61, 55.21, 56.27, 68.54, 71.25, 117.66, 139.74.

(25S)-Cholest-7-ene-3-one-26-al (S-XXIII)

¹H NMR: δ 0.54 (s, 3H), 0.86-0.94 (m, 5H), 0.99 (s, 4H), 1.05-1.11 (m, 5H), 1.14-1.90 (m, 36H), 1.94-2.17 (m, 3H), 2.17-2.50 (m, 6H), 5.14-5.20 (m, 1H), 9.53-9.63 (m, 1H);

¹³C NMR: δ 12.12, 12.69, 13.69, 19.01, 21.90, 23.14, 23.74, 28.17, 30.26, 31.26, 34.60, 36.08, 36.28, 38.35, 38.97, 39.61, 43.06, 43.58, 44.46, 46.64, 49.02, 55.11, 56.15, 117.27, 139.68, 205.76, 212.34.

(25S)-Cholest-7-ene-3-one-26-oic acid (Δ^7 -dafachronic acid, S-I)

$[\alpha]_D^{25} +21.0$ (c 2.0, CDCl₃) cf. Lit. $+23.4$ (c 2.0, CDCl₃) (2).

¹H NMR: δ 0.54 (s, 3H), 0.86-0.94 (m, 5H), 1.00 (s, 4H), 1.10-1.31 (m, 14H), 1.31-1.92 (m, 27H), 1.94-2.17 (m, 3H), 2.17-2.52 (m, 6H), 5.14-5.19 (m, 1H).

¹³C NMR: δ 12.10, 12.67, 17.24, 18.95, 21.88, 23.12, 23.90, 23.99, 28.12, 29.91, 30.23, 34.08, 34.22, 34.57, 35.87, 36.25, 38.32, 38.95, 39.59, 43.03, 43.55, 44.43, 48.99, 55.09, 56.20, 76.80, 111.21, 139.68, 182.81, 212.45.

Δ^4 Series

(25R)-Cholest-4-ene-3-one-26-al (XXV)

^1H NMR: δ 0.69 (s, 3H), 0.84-0.94 (m, 5H), 0.95-1.74 (m, 30H), 1.75-1.88 (m, 2H), 1.93-2.03 (m, 2H), 2.18-2.47 (m, 6H), 5.70 (bs, 1H) [olefin C-4], 9.56 (d, 1H, $J=1.83$ Hz);
 ^{13}C NMR: δ 11.22, 12.56, 16.64, 17.84, 20.27, 22.65, 23.42, 27.45, 30.14, 31.29, 32.20, 33.24, 34.85, 34.94, 35.07, 37.86, 38.86, 41.65, 45.62, 53.04, 55.11, 55.21, 123.00 [olefin C-4], 170.96 [olefin C-5], 198.92, 204.67.

(25R,S)-Cholest-4-ene-3-one-26-al (R/S-XXV)

^1H NMR: δ 0.68 (s, 3H), 0.84-1.13 (m, 12H), 1.16 (s, 3H), 1.20-1.72 (m, 14H), 1.74-1.89 (m, 2H), 1.94-2.06 (m, 2H), 2.20-2.47 (m, 6H), 5.70 (bs, 1H), 9.58-9.61 (m, 1H) [aldehyde, pseudo-triplet];
 ^{13}C NMR: δ 11.21, 12.56, 12.73, 16.64, 17.84, 20.27, 22.65, 22.70, 23.41, 27.45, 30.14, 30.30, 31.28, 32.19, 33.24, 34.85, 34.94, 35.07, 35.15, 37.85, 38.85, 41.65, 45.61, 45.65, 53.03, 55.10, 55.20, 123.00, 170.96, 198.92, 204.69.

(25R,S)-Cholest-4-ene-3,26-diol (XXVI)

^1H NMR: δ 0.66 (s, 3H), 0.84-1.49 (m, 30H), 1.49-1.87 (m, 12H), 1.87-2.07 (m, 3H), 2.1-2.24 (m, 1H), 3.34-3.54 (m, 2H), 4.06-4.19 (m, 1H), 5.23 (m, 1H).

(25S)-Cholest-4-ene-26-acetoxy-3-ol (XXVII)

^1H NMR: δ 0.66 (s, 3H), 0.79-1.86 (m, 36H), 1.86-2.08 (m, 6H), 2.09-2.25 (m, 1H), 3.74-3.98 (m, 2H), 4.07-4.18 (m, 1H), 5.23 (bs, 1H).

(25S)-Cholest-4-ene-3,26-diol (S-XXVI)

^1H NMR: δ 0.66 (s, 3H), 0.84-1.00 (qt, 9H, $J=2.9$ Hz), 1.03 (s, 3H), 1.06-1.87 (m, 24H), 1.89-2.07 (m, 3H), 2.11-2.26 (m, 1H), 3.40 (dd, 1H, $J=10.6, 6.41$ Hz), 3.49 (dd, 1H, $J=10.6, 5.6$ Hz), 5.23-5.29 (m, 1H).

(25S)-Cholest-4-ene-3-one-26-oic acid (Δ^4 -dafachronic acid, S-II)

$[\alpha]_D +19.88$ (c 0.2, CDCl_3)

^1H NMR: δ 0.69 (s, 3H), 0.889 (d, 3H, $J=6.6$ Hz), 1.12-1.20 (m, 8H), 1.21-1.50 (m, 9H), 1.46-1.74 (m, 6H), 1.74-1.88 (m, 2H), 1.94-2.06 (m, 2H), 2.20-2.50 (m, 6H), 5.71 (bs, 1H).
 ^{13}C NMR: δ 12.15, 17.23, 17.57, 18.76, 21.21, 23.82, 23.92, 24.36, 28.37, 32.22, 33.16, 34.09, 34.15, 34.21, 35.79, 35.85, 38.80, 39.59, 39.79, 42.59, 53.97, 56.03, 56.20, 123.92, 172.12, 182.76, 200.09.

Δ^5 Series

(25RS)-Cholest-5-ene-3 β -tert-butyltrimethylsilyloxy-26-al (R/S-XII)

^1H NMR: δ -0.045 (s, 6H), 0.69 (s, 3H), 0.78-1.16 (m, 16H), 1.17-1.90 (m, 26H), 3.41-3.52 (m, 1H), 5.27-5.33 (m, 1H), 9.58-9.62 (m, 1H) [aldehyde, pseudo-triplet].

(25R)-Cholest-5-ene-3 β -tert-butyltrimethylsilyloxy-26-ol (R/S-XIII)

¹H NMR: δ -0.043 (s, 6H), 0.66 (s, 3H), 0.78-1.64 (m, 48H), 1.64-1.89 (m, 4H), 1.90-2.08 (m, 2H), 2.10-2.36 (m, 2H), 3.32-3.59 (m, 3H), 5.27-5.35 (m, 1H).

(25S)-Cholesta-3 β -tert-butyltrimethylsilyloxy-26-acetoxy-5-ene (XXVIII)

¹H NMR: δ -0.043 (s, 6H), 0.66 (s, 3H), 0.80-1.70 (m, 54H), 1.64-1.89 (m, 4H), 1.9-2.02 (m, 2H), 2.02-2.11 (m, 3H), 2.1-2.36 (m, 2H), 3.46 (qt, 1H, J=5.07 Hz), 3.82 (dd, 1H, J=10.54, 6.83 Hz), 3.94 (dd, 1H, J=10.93, 5.85 Hz), 5.26 (m, 1H).

(25S)-Cholesta-5-ene-3 β -tert-butyltrimethylsilyloxy-26-ol (S-XIII)

¹H NMR: δ 0.044 (s, 6H), 0.66 (s, 3H), 0.76-1.65 (m, 52H), 1.65-1.88 (m, 3H), 1.88-2.09 (m, 2H), 2.09-2.38 (m, 2H), 3.36-3.52 (m, 3H), 5.25-5.35 (m, 1H).

(25S)-Cholest-5-ene-3 β -tert-butyltrimethylsilyloxy-26-oic acid (S-XV)

¹H NMR: δ -0.043 (s, 6H), 0.65 (s, 3H), 0.78-1.30 (m, 50H), 1.30-1.87 (m, 22H), 1.87-2.08 (m, 2H), 2.38 (m, 1H), 3.46 (qt, 1H, J=5.07 Hz), 5.25-5.35 (m, 1H).

(25S)-Cholest-5-ene-3 β -ol-26-oic acid (S-XVI)

¹H NMR: δ 0.66 (s, 3H), 0.77-0.96 (m, 5H), 0.96-1.74 (m, 28H), 1.74-1.89 (m, 2H), 1.89-2.06 (m, 2H), 2.16-2.34 (m, 2H), 2.38 (m, 1H), 3.41-3.58 (m, 1H), 5.26-5.38 (m, 1H).

(25S)-Cholest-5-ene-3-keto-26-acid (S-III)

¹H NMR: δ 0.69 (s, 3H), 0.71-0.97 (m, 4H), 1.10-1.76 (m, 28H), 1.76-1.90 (m, 2H), 1.90-2.50 (m, 6H), 5.28-5.37 (m, 1H) [olefin C-6].

Scheme 5

(25R)-5 α -Cholest-26-ol-3-one (XXIX)

¹H NMR: δ 1.03 (s, 3H), 1.06-2.10 (m, 38H) [contains 5 α -proton ~1.64], 2.10-2.80 (m, 8H), 2.98-3.12 (m, 1H), 3.71-3.93 (m, 2H).

(25R)-5 α -Cholest-3-one-26-oic acid (IV)

¹H NMR: δ 0.67 (s, 3H), 0.78-0.94 (m, 4H), 0.94-1.93 (m, 28H) [contains 5 α -proton], 1.93-2.07 (m, 3H), 2.07-2.52 (m, 6H), 2.62-2.76 (m, 1H).

^{13}C NMR: δ 11.70, 12.29, 17.01, 18.81, 21.65, 23.85, 24.44, 26.01, 28.46, 29.18, 29.93, 31.93, 34.15, 35.60, 35.86, 38.43, 38.78, 40.10, 44.57, 44.96, 46.92, 53.99, 56.39, 56.47, 56.67, 182.22, 213.89.

(25R)-5 β -Cholest-3-one-26-oic acid (V)

^1H NMR: δ 0.59-0.69 (m, 3H), 0.70-1.74 (m, 36H) [contains 5 β -proton], 1.75-1.90 (m, 2H), 1.90-2.10 (m, 3H), 2.10-2.50 (m, 3H), 2.68 (t, $J=13.4\text{Hz}$, 1H).

^{13}C NMR: δ 12.27, 16.97, 18.81, 21.40, 22.87, 23.84, 24.39, 25.99, 26.83, 28.49, 34.11, 35.10, 35.73, 35.83, 35.90, 37.23, 37.44, 39.38, 40.27, 40.92, 42.59, 42.94, 44.56, 56.44, 56.65, 182.05, 213.87.

(25S)-5 α -Cholest-3,26-diol (S-XXX)

^1H NMR: δ 0.66 (s, 3H), 0.82-2.10 (m, 36H) [contains 5 α -proton], 2.20-2.40 (m, 2H), 3.40-3.58 (m, 3H).

(25S)-5 α -Cholest-3-one-26-oic acid (S-IV)

^1H NMR: δ 0.58-0.68 (m, 3H), 0.78-0.96 (m, 12H), 1.16-1.94 (m, 24H) [contains 5 α -proton], 1.94-2.20 (m, 4H), 2.21-2.54 (m, 3H), 2.64-2.74 (m, 1H).

(25S)-5 β -Cholest-3-one-26-oic acid (S-V)

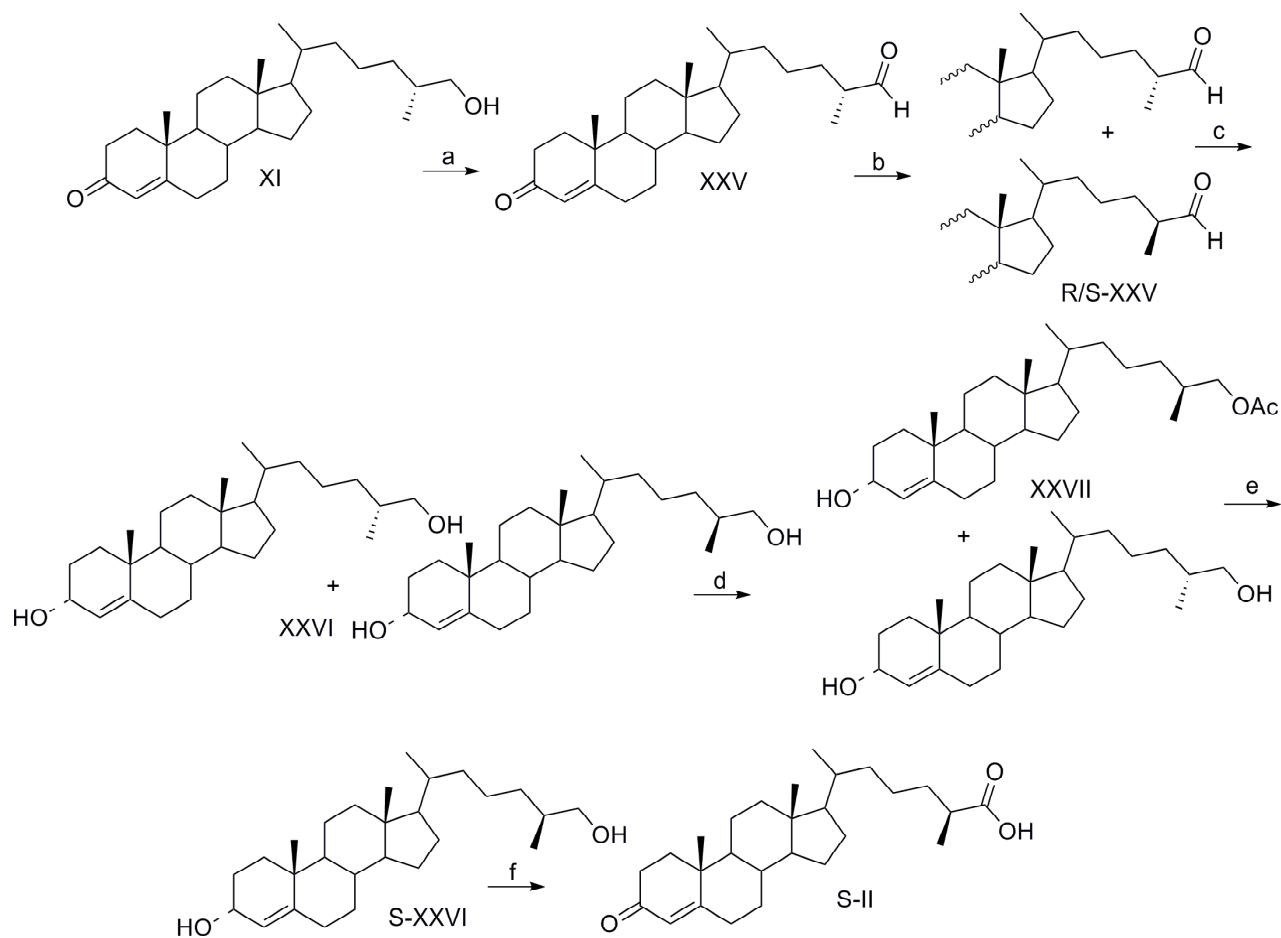
^1H NMR: δ 0.69 (s, 3H), 0.79-1.78 (m, 30H) [contains 5 β -proton], 1.78-2.54 (m, 12H), 2.62-2.76 (m, 1H).

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1. **Giroux S, Corey EJ** 2008 An efficient, stereocontrolled synthesis of the 25-(R)-diastereomer of dafachronic acid A from β -ergosterol. *Org Lett* 10:801-802
2. **Giroux S, Corey EJ** 2007 Stereocontrolled synthesis of dafachronic acid A, the ligand for the DAF-12 nuclear receptor of *Caenorhabditis elegans*. *J Am Chem Soc* 129:9866-9867
3. **Martin R, Dabritz F, Entchev EV, Kurzchalia TV, Knolker HJ** 2008 Stereoselective synthesis of the hormonally active (25S)- Δ^7 -dafachronic acid, (25S)- Δ^4 -dafachronic acid, (25S)-dafachronic acid, and (25S)-cholestenoic acid. *Org Biomol Chem* 6:4293-4295

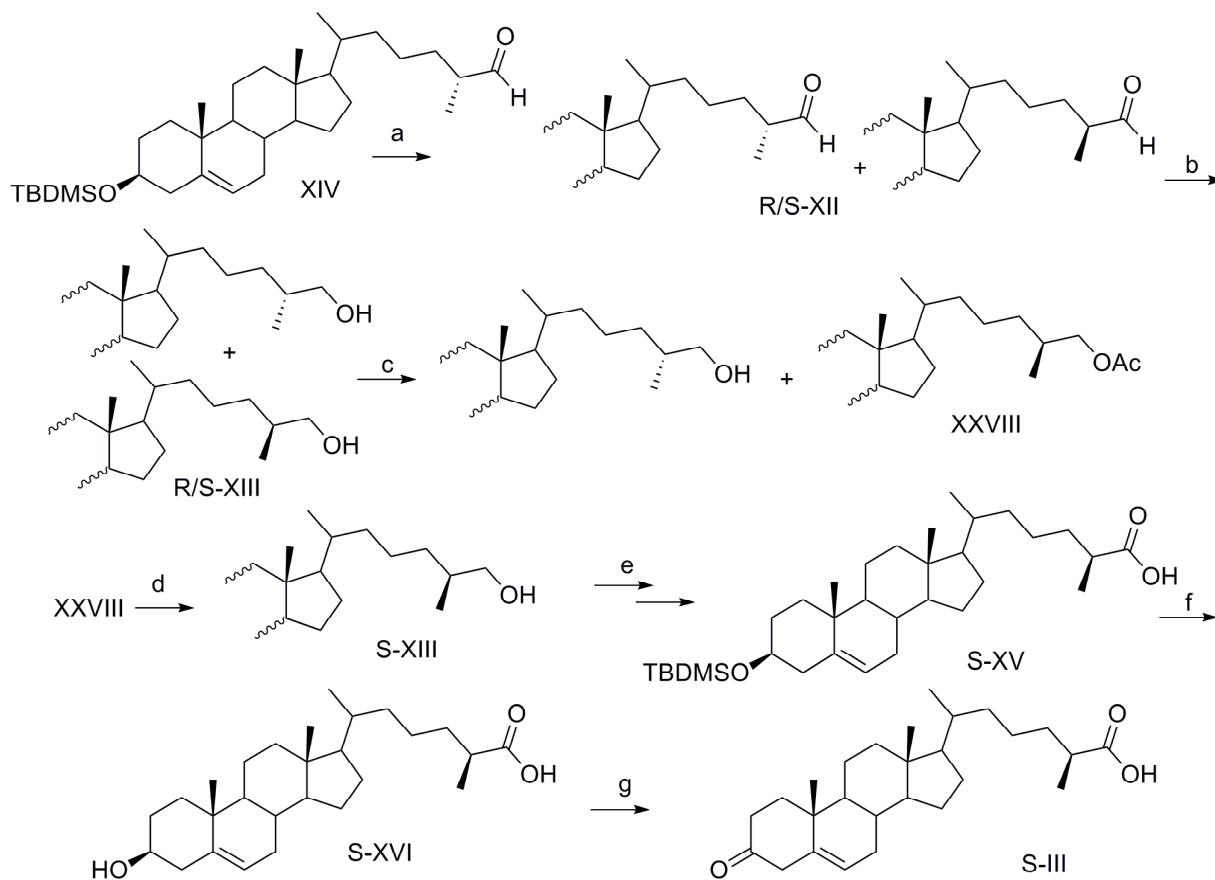
Schemes 4a and 4b

Scheme 4a



(a) PCC, NaOAc, CH₂Cl₂ (b) DBU, THF, 24h, (c) NaBH₄, Methanol, 0 C (d) *Pseudomonas cepacia* lipase, vinyl acetate, CHCl₃ (e) KOH, MeOH, Reflux (f) Jones reagent, 0 C

Scheme 4b



(a) DBU, THF, 24h (b) NaBH₄, MeOH, 0 C (c) *Pseudomonas cepacia* lipase, vinyl acetate, CHCl₃ (d) KOH, MeOH (e) i) Dess-Martin periodinane, CH₂Cl₂ ii) NaClO₂, NaH₂PO₄, 2-Methyl-2-butene (f) TBAF, THF (g) IBX, DMSO.

These schemes describe the conversion of the 25(R) isomers to the 25(S) isomers in the Δ^4 and Δ^5 series (Scheme 4a) or the 5 α - and 5 β - series (Scheme 4b).