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7,8-Dihydro Analogs of Ecdysteroids*

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Abstract—Reactions of 20-hydroxyecdysone, its diacetonide, and 24,25(25,26)-anhydro derivative with lithium tetrahydridoaluminate gave the corresponding 6α- and 6β-epimeric alcohols and 7,8-dihydro analogs.

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Selective reduction of the double Δ^7-bonds in ecdysteroids with formation of 7,8-dihydro analogs opens a way to new biologically active structures. Catalytic hydrogenation of ecdysteroids does not produce the desired products because of numerous side reactions [2–4]. Suksamrarn et al. [5] recently reported on stereoselective catalytic hydrogenation of Δ^7-6-oxo steroids in the presence of sodium nitrite; however, we failed to obtain 7,8-dihydro analogs from 20-hydroxyecdysone and its derivatives according to the procedure described in [5]. Our attempts to hydrogenate the Δ^7-bond in 20-hydroxyecdysone and its derivatives via reaction with alkali metals in liquid ammonia [6, 7] (which is used for selective reduction of double bond in conjugated ketones of the steroid series) were also unsuccessful.

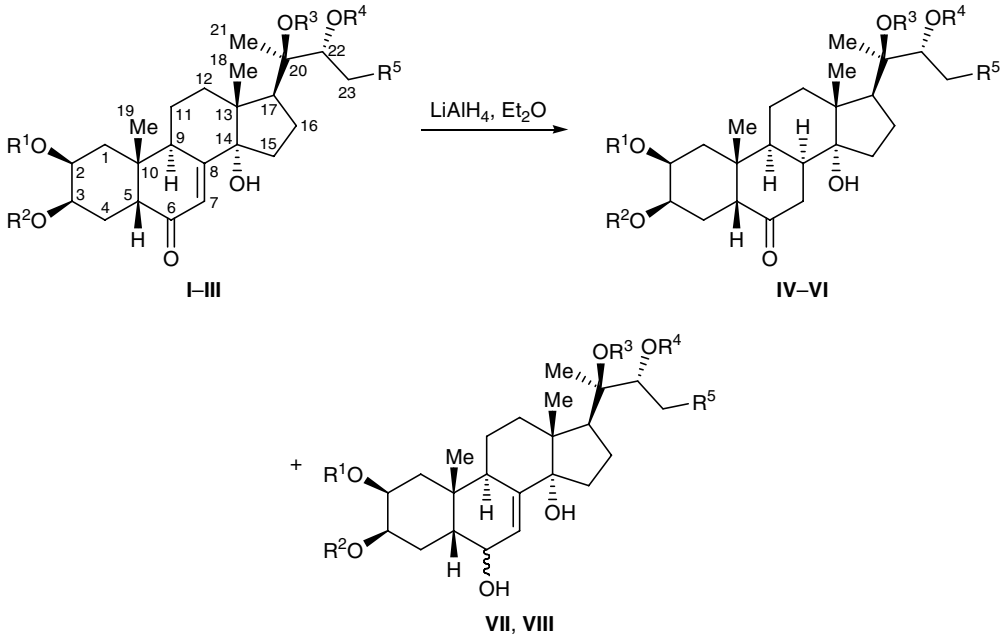
While studying the reactions of 20-hydroxyecdysone (**I**), its 2,3:20,22-diacetonide **II** and 24,25-(25,26)-anhydro-20-hydroxyecdysone diacetonide **III** (a 3:2 mixture of Δ^{24} and Δ^{25} derivatives) with lithium tetrahydridoaluminate we revealed formation of the corresponding 7,8-dihydro analogs **IV**–**VI** (Scheme 1). In the reaction of compound **I** with $LiAlH_4$ at a molar ratio of 1:7 (a suspension in diethyl ether) we isolated 21% of 7,8-dihydro analog **IV** which was identical in the IR and NMR (^1H and ^{13}C) spectra to a sample described previously [5]. The reactions of diacetonides **II** and **III** with 3 equiv of $LiAlH_4$ gave the corresponding 7,8-dihydro analogs **V** and **VI** in 35 and 30% yield, respectively. In addition, we isolated mixtures (~1:2) of previously described [8] 6α/6β-epimeric alcohols **VII** and **VIII**, whose yields were 60 and 65%, respectively. When the reaction with diacetonide **II** was carried out by adding $LiAlH_4$ to a solution of **II** (i.e., the order of mixing the reactants was changed), ~10% of compound **IX** was formed together with **V** and **VII**. The reaction with 5 equiv of $LiAlH_4$ gave rise to a mixture of compounds **V**, **VII**, and **X** (Scheme 2).

It could be presumed that 7,14-diene **IX** is formed via dehydration of alcohol **VII** and that $\Delta^{14(15)}$-alcohol **X** is the product of reduction and dehydration of 7,8-dihydro derivative **V**. However, compounds **IX** and **X** were not obtained in the reactions of alcohols **VII** and **V** with $LiAlH_4$. In these cases, alcohol **VII** was recovered from the reaction mixture, while the reaction of ketone **V** with $LiAlH_4$ afforded the corresponding alcohol **XI** which failed to react with $LiAlH_4$. Therefore, we concluded that compounds **IX** and **X** were formed from a common precursor.

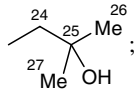
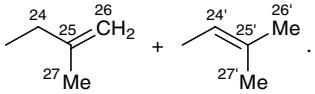
The ^{13}C NMR spectra of saturated ketones **IV**–**VI** displayed characteristic differences from the spectra of initial conjugated enones **I**–**III**. The C^7 and C^8 signals appeared in a considerably stronger field, while the C^6 signal was displaced downfield ($\Delta\delta_C$ ~9 ppm) due to the lack of conjugation between the carbonyl group and double bond. Signals in the ^1H and ^{13}C NMR spectra of ketone **V** and alcohol **XI** were assigned using homo- and heteronuclear correlation techniques (COSY, HSQC, HMBC, TOCSY, ROESY). ROESY experiments showed nuclear Overhauser effect between protons of the β-oriented $C^{19}H_3$ group and 5-H

* For preliminary communication, see [1].

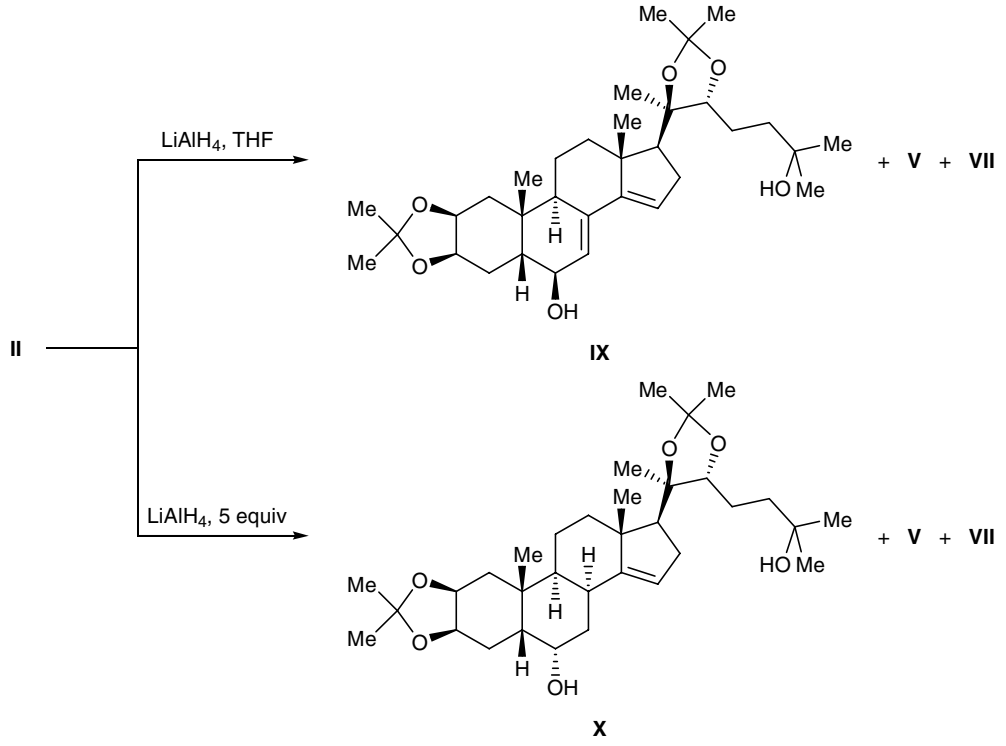
Scheme 1.



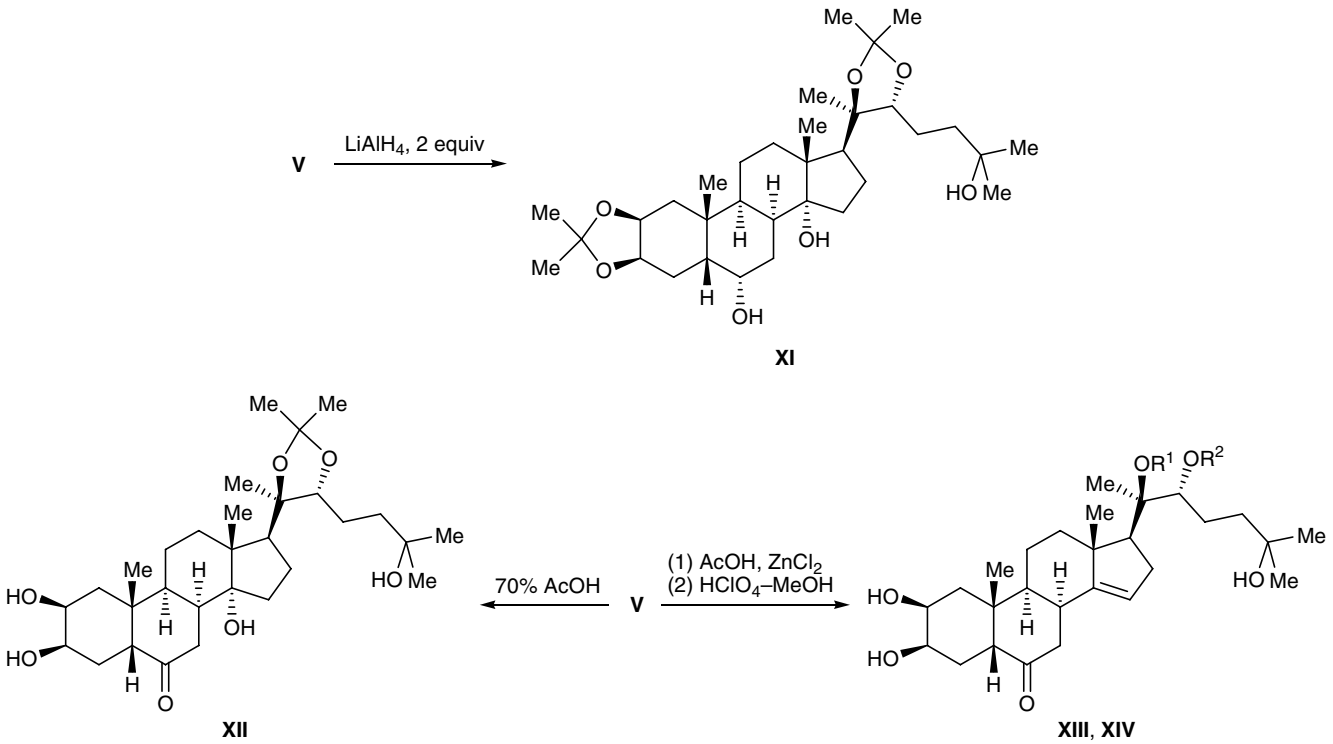
I, **IV**, $R^1 = R^2 = R^3 = R^4 = H$; **II**, **III**, **V**–**VIII**, $R^1R^2 = R^3R^4 = Me_2C$.

I, **II**, **IV**, **V**, **VII**, R^5 =  ; **III**, **VI**, **VIII**, R^5 =  .

Scheme 2.

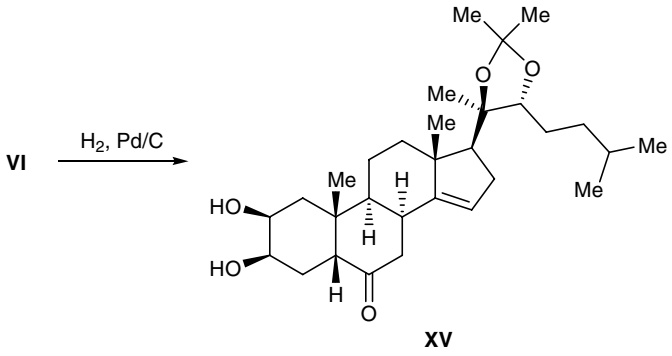


Scheme 3.



XIII, $R^1R^2 = Me_2C$; **XIV**, R^1, $R^2 = H$.

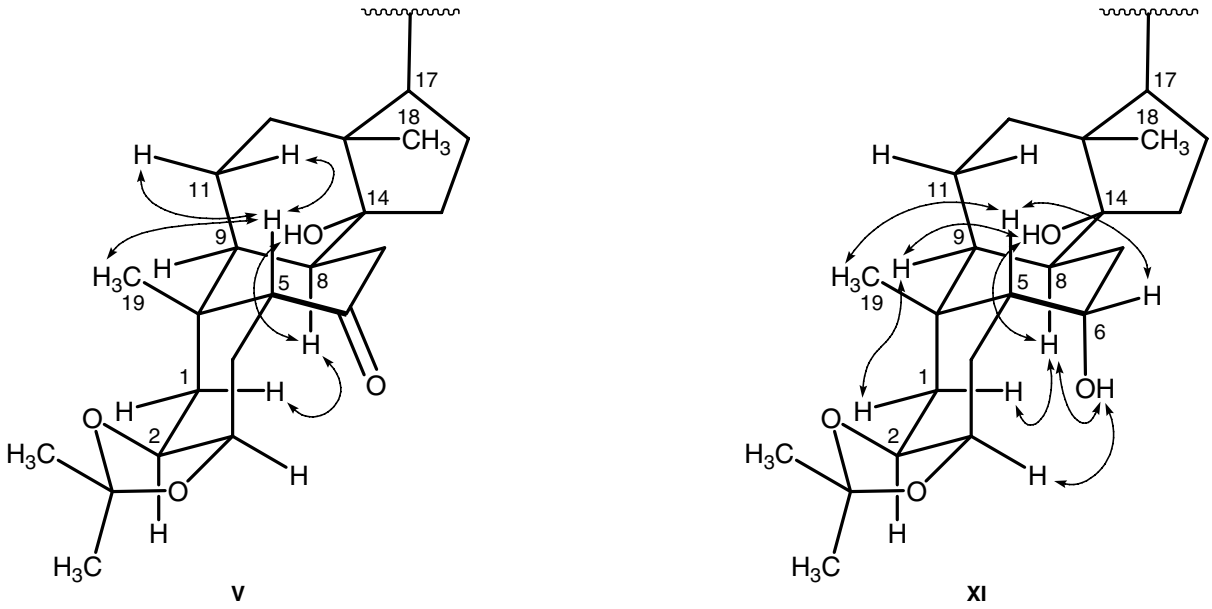
Scheme 4.



in molecule **V**, indicating *cis*-junction of the A and B rings, i.e., β-orientation of 5-H. The existence of NOE between 8-H and α-14-OH (ROESY) confirmed α-orientation of the former (see figure).

These data show that hydride reduction of the Δ^7-bond in diacetonide **II** is not accompanied by epimerization at C^5 and that the attack by hydride ion on the double-bonded C^8 atom occurs at the α-side. Unlike α,β-unsaturated ketone **II** [8], no epimerization at C^5 was observed in the hydride reduction of the ketone group in unsaturated ketone **V**. The reduction of ketone **V** with lithium tetrahydridoaluminate is stereospecific, and the product is 6α-alcohol **XI** (Scheme 3), while the reduction of the 6-oxo group in compound **II** under the same conditions gives a 1:2 mixture of 6α- and 6β-epimeric alcohols **VII** [8].

The structure of alcohol **XI** (see figure) was determined on the basis of NOE cross peaks observed in the ROESY spectra. β-Orientation of the 5-H proton follows from the existence of a correlation between that proton and protons of the $C^{19}H_3$ group (HMBC). Couplings between the 14-OH proton, on the one hand, and 8-H and 9-H, on the other, suggests α-configuration of the newly formed chiral center at C^8, and a strong cross peak between 5-H and 6-H unambiguously indicates β-orientation of the latter and hence



Cross couplings (NOEs) in the ROESY experiments for compounds **V** and **XI**.

formation of 6α-epimeric alcohol **XI**. An additional support to the α-orientation of the 6-OH group is provided by the presence of a cross peak between the 6-OH proton and 8-H. Interaction between the 6α-OH proton and 3-H was also observed; this means that the latter occupies axial position; correspondingly, the 2-H proton is oriented equatorially.

As follows from our data on the stereochemistry of hydride reduction, the known C^5-epimerization of ecdysteroids under alkaline conditions [9, 10] accompanies the reduction of the 6-oxo group in Δ^7-6-oxo ecdysteroids; as a result, 6-hydroxy derivatives of the 5α-series are formed [8]. The hydride reduction of the Δ^7-bond in Δ^7-6-oxo ecdysteroids **I**–**III** gives rise to 7,8-dihydro derivatives **IV**–**VI** of the 5β-series. Likewise, no epimerization at C^5 is observed in the hydrogenation of the oxo group in saturated ketone **V**. We can conclude that 5β-epimers of 7,8-dihydro-6-oxo and 7,8-dihydro-6-hydroxy ecdysteroid derivatives with *cis*-junction of the A and B rings are more stable.

The structure of 7,14-dien-6β-ol **IX** is confirmed by comparison of its ^{1}H and ^{13}C NMR spectra with those of the corresponding 6α-epimer [8]. Signals from C^5 and C^6 in the ^{13}C NMR spectrum of the former appear in a weaker field ($\Delta\delta_C$ = 1.8 and 4.1 ppm, respectively, while the C^7 signal is displaced upfield ($\Delta\delta_C$ = 1.0 ppm; the C^7 and C^{15} signals were misassigned in [8]). The 6-H signal in the ^{1}H NMR spectrum of 6β-dienol **IX** is located in a stronger field ($\Delta\delta$ = 0.76 ppm) relative to the corresponding signal of the 6α-epimer (cf. the data for 6α- and 6β-epimeric alcohols **VII** [8]).

The presence of double C^{14}=C^{15} bond in alcohol **X** induces appreciable changes in the ^{1}H and ^{13}C NMR spectral patterns as compared to saturated alcohol **XI**. The ^{1}H NMR spectrum of **X** contains a signal at δ 5.35 ppm from the vinyl proton on C^{15}, and the C^{14} and C^{15} sp^2-hybridized carbon atoms give rise to downfield signals at δ_C 154.4 and 120.6 ppm, respectively, in the ^{13}C NMR spectrum. The C^8, C^{12}, C^{16}, and C^{17} signals are displaced downfield ($\Delta\delta_C$ = 11.5, 7.4, 7.0, and 9.7 ppm, respectively), while the C^9 signal is located in a stronger field ($\Delta\delta_C$ = 11.3 ppm). As follows from the Dreiding model, the C^8, C^{16}, and C^{17} atoms in molecule **X** lie in the C^{14}=C^{15} bond plane and are therefore deshielded, while the C^9 atom falls into the shielded area (out of the double bond plane) [11].

Hydrolysis of diacetonide **V** in 70% acetic acid or AcOH/$ZnCl_2$ [12] resulted in deprotection of only hydroxy groups on C^2 and C^3; the reaction in the presence of $ZnCl_2$ was accompanied by dehydration to generate $\Delta^{14(15)}$-bond. As a result, 20,22-acetonides **XII** and **XIII** were obtained, respectively. Deprotection of all four hydroxy groups was achieved using perchloric acid in methanol [13]. In this case, the reaction was also accompanied by dehydration, and the product was enone **XIV** (Scheme 3).

The formation of $\Delta^{14(15)}$ bond also occurred in the catalytic hydrogenation of the side-chain double bond of Δ^{24}(Δ^{25})-alkenes **VI**. The reaction was accompanied by deprotection of the hydroxy groups on C^2 and C^3 to give enone **XV** (Scheme 4). An analogous process was

described in [4]. Deprotection of the 2,3-dihydroxy moiety is readily identified by the ^{13}C NMR spectra of compounds **XII**, **XIII**, and **XV**, which contain only one acetal signal at δ_C 106.8 ppm. Deshielding effect of the $\Delta^{14(15)}$-bond leads to downfield shift of the 8-H and 17-H signals in the ^1H NMR spectra of compounds **XIII** and **XV**; as a result, these signals appear in the region free from other signals, and they show a clearly defined fine structure. The 8-H signal is a doublet of triplets ($J_{8,7\beta}$ = 14.0, $J_{8,9}$ = 4.0 Hz) at δ 3.03 (**XIII**) and 3.04 ppm (**XV**), and the 17-H signal is a doublet of doublets (J = 14.5, 11.0 Hz) at δ 2.48 ppm.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples dispersed in mineral oil. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 instrument (300.13 for ^1H and 75.46 MHz for ^{13}C) using $CDCl_3$ and CD_3OD as solvents. Homo- and heteronuclear COSY, TOCSY, ROESY, HSQC, and HBMC experiments were run on a Bruker DRX-500 spectrometer (500.13 MHz for ^1H and 125.76 MHz for ^{13}C) using DMSO as solvent; to identify hydroxy groups, samples were subjected to lyophilization. The chemical shifts were measured relative to tetramethylsilane as internal reference. The melting points were determined on a Boetius melting point apparatus. The specific rotations were measured on a Perkin–Elmer 141 polarimeter. Thin-layer chromatography was performed on silica gel (Silufol plates); spots were visualized by treatment with a solution of vanillin in ethanol acidified with sulfuric acid.

(20*R*,22*R*)-2β,3β,14α,20,22,25-Hexahydroxy-7,8α-dihydro-5β-cholestan-6-one (IV, 7,8α-dihydro-20-hydroxyecdysone). A suspension of 0.5 g (1.04 mmol) of 20-hydroxyecdysone **I** (mp 246°C; prepared according to the procedure described in [14]) in 20 ml of diethyl ether was added under argon to a suspension of 0.277 g (7.29 mmol) of $LiAlH_4$ in 30 ml of diethyl ether, cooled to ~0°C. The mixture was stirred for 30 min at room temperature, 10 ml of methanol was added, the mixture was stirred for 2 h and cooled to 0°C, 5 ml of water was added, and the mixture was neutralized with 5% hydrochloric acid (~13 ml) to a weakly acidic reaction. The mixture was evaporated under reduced pressure to a volume of ~20 ml and extracted with ethyl acetate (3×50 ml). The extract was evaporated under reduced pressure, and the residue was subjected to chromatography on 15 g of silica gel using chloroform–methanol (10:1) as eluent. Yield 0.103 g (21%), R_f 0.52 ($CHCl_3$–MeOH, 5:1), mp 138–140°C, $[\alpha]_D^{17}$ = +24.5° (c = 3.47, MeOH) (cf. [5]). The IR and ^1H and ^{13}C NMR spectra of the product were identical to those given in [5].

(20*R*,22*R*)-14α,25-Dihydroxy-2β,3β:20,22-bis(isopropylidenedioxy)-5β,8a-cholestan-6-one (V, 7,8α-dihydro-20-hydroxyecdysone 2,3:20,22-diacetonide). A solution of 0.82 g (1.46 mmol) of diacetonide **II** (mp 234°C; prepared as described in [15]) in 25 ml of diethyl ether was added under stirring in an argon atmosphere to a suspension of 0.16 g (4.39 mmol) of $LiAlH_4$ in 25 ml of diethyl ether, cooled to ~0°C. The mixture was stirred for 1 h at room temperature, cooled to 0°C, and 3 ml of water and ~5 ml of 5% hydrochloric acid (to a weakly acidic reaction) were added. The ether layer was separated, and the aqueous layer was extracted with ethyl acetate (3×30 ml). The extracts were combined with the organic phase and evaporated under reduced pressure, and the residue was subjected to chromatography on 5 g of silica gel using chloroform as eluent to isolate 0.29 g (35%) of compound **V**, R_f 0.63 ($CHCl_3$–MeOH, 10:1), and 0.49 g (60%) of previously described [8] alcohols **VII** {In the ^{13}C NMR spectrum given in [8], signals from C^{24}, δ_C 39.6 and 39.2 ppm, respectively, for the 6α- and 6β-epimers of **VII** were missing}.

Compound **V**. mp 275–277°C, $[\alpha]_D^{19}$ = +14.2° (c = 11.97, $CHCl_3$). IR spectrum: ν(C=O) 1700 cm^{-1}. ^1H NMR spectrum, δ, ppm: in $CDCl_3$: 1.07 s (3H, $C^{18}H_3$), 1.10 s (3H, $C^{21}H_3$), 1.19 s (6H, $C^{26}H_3$, $C^{27}H_3$), 1.35 s (3H, $C^{19}H_3$), 1.26 s, 1.27 s, 1.38 s, 1.47 s (12H, Me_2C), 1.54–2.09 m (17H, CH, CH_2), 2.16 m (1H, 7α-H), 2.29 m (1H, 17-H), 2.33 d.t (1H, 8-H, $J_{8,7\beta}$ = 13.5, $J_{8,7\alpha}$ = $J_{8,9}$ = 4.0 Hz), 2.55 br.s (1H, 5-H, $w_{1/2}$ = 8.9 Hz), 2.68 t (1H, 7β-H, $J_{7\beta,7\alpha}$ = $J_{7\beta,8}$ = 13.4 Hz), 3.62 m (1H, 22-H, $w_{1/2}$ = 13.0 Hz), 4.17 m (1H, 2-H, $w_{1/2}$ = 12 Hz), 4.45 m (1H, 3-H, $w_{1/2}$ = 21 Hz); in DMSO-d_6 (500.13 MHz): 1.02 s (3H, $C^{18}H_3$), 1.05 s (3H, $C^{21}H_3$), 1.07 s (3H, $C^{27}H_3$), 1.08 s (3H, $C^{26}H_3$), 1.16 m and 1.76 m (2H, 15-H), 1.19 s and 1.39 s (6H, 2,3-Me_2C), 1.23 s and 1.32 s (6H, 20,22-Me_2C), 1.28 s (3H, $C^{19}H_3$), 1.34 m and 1.55 m (2H, 24-H), 1.36 m and 1.39 m (2H, 23-H), 1.38 s and 1.99 s (2H, 4-H), 1.52 m and 1.67 m (2H, 1-H), 1.62 m and 1.81 m (2H, 12-H), 1.64 m and 1.77 m (2H, 11-H), 1.69 m and 1.81 m (2H, 16-H), 1.98 d.t (1H, 9-H, J = 11.0, 4.0 Hz), 2.06 d.d (1H, 7α-H, $J_{7\alpha,8}$ = 4.0, $J_{7\alpha,7\beta}$ = 13.0 Hz), 2.20 m (1H, 17-H), 2.68 br.s (1H, 5-H, $w_{1/2}$ = 2 Hz), 2.71 t (1H, 7β-H, $J_{7\beta,7\alpha}$ = $J_{7\beta,8}$ = 13.0 Hz), 3.30 d.t (1H, 8-H, $J_{8,7\beta}$ = 13.0, $J_{8,7\alpha}$ = $J_{8,9}$ = 4.0 Hz),

3.57 m (1H, 22-H), 3.92 s (1H, 14-OH), 4.13 s (1H, 25-OH), 4.14 m (1H, 2-H), 4.27 m (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: in $CDCl_3$: 18.1 t (C^{11}), 18.4 q (C^{18}), 21.0 t (C^{16}), 21.3 q (C^{21}), 23.5 t (C^{23}), 25.3 t (C^4), 26.7 q (C^{19}), 25.8 q and 28.4 q (2,3-**Me**$_2$C), 26.7 q and 28.9 q (20,22-**Me**$_2$C), 29.0 q (C^{27}), 29.6 q (C^{26}), 31.3 t (C^{15}), 33.1 t (C^{12}), 34.2 t (C^1), 39.5 s (C^{10}), 41.3 t (C^{24}), 41.3 t (C^7), 41.5 d (C^9), 43.7 d (C^8), 46.8 s (C^{13}), 49.7 d (C^{17}), 50.5 d (C^5), 70.2 s (C^{25}), 70.8 d (C^3), 73.5 d (C^2), 81.8 d (C^{22}), 84.4 s (C^{14}), 84.9 s (C^{20}), 106.8 s (20,22-Me$_2$**C**), 107.6 s (2,3-Me$_2$**C**), 212.1 s (C^6); in DMSO (500.13 MHz): 17.8 t (C^{11}), 18.0 q (C^{18}), 21.0 t (C^{16}), 21.4 q (C^{21}), 23.1 t (C^{23}), 25.3 t (C^4), 25.9 q (C^{19}), 25.9 q and 28.5 q (2,3-**Me**$_2$C), 26.6 q and 29.0 q (20,22-**Me**$_2$C), 29.0 q (C^{27}), 29.7 q (C^{26}), 30.1 t (C^{15}), 32.8 t (C^{12}), 33.8 t (C^1), 38.9 s (C^{10}), 40.8 t (C^7), 40.9 d (C^9), 41.1 t (C^{24}), 42.7 d (C^8), 46.3 s (C^{13}), 49.3 d (C^{17}), 49.5 d (C^5), 68.4 s (C^{25}), 70.2 d (C^3), 73.0 d (C^2), 81.3 d (C^{22}), 82.8 s (C^{14}), 84.1 s (C^{20}), 105.8 s (20,22-Me$_2$**C**), 106.8 s (2,3-Me$_2$**C**), 211.9 s (C^6).

(20*R*,22*R*)-14α-Hydroxy-2β,3β:20,22-bis(isopropylidenedioxy)-5β,8α-cholest-24(25)-en-6-ones [VI, 24,25(25,26)-anhydro-7,8α-dihydro-20-hydroxyecdysone 2,3:20,22-diacetonides] (mixture of isomers)**.** A solution of 1.3 g (2.40 mmol) of isomeric alkenes **III** (prepared as described in [12, 16]) in 30 ml of diethyl ether was added under stirring in an argon atmosphere to a suspension of 0.27 g (7.2 mmol) of $LiAlH_4$ in 30 ml of diethyl ether, cooled to ~0°C. The mixture was stirred for 3 h at room temperature, cooled to 0°C, 5 ml of water was added, and ~10 ml of 5% hydrochloric acid was added to a weakly acidic reaction. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×50 ml). The extracts were combined with the organic phase and evaporated under reduced pressure, and the residue was subjected to chromatography on 30 g of silica gel using chloroform as eluent to isolate 0.39 g (30%) of compound **VI**, R_f 0.5 ($CHCl_3$–MeOH, 20:1), and 0.85 g (65%) of previously described [8] alcohols **VIII**.

Compound (**VI**). mp 190–192°C, $[\alpha]_D^{19}$ = +16.1° (c = 8.83, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1695 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.91 s and 0.96 s (3H, $C^{18}H_3$, $C^{18'}H_3$); 0.94 s (3H, $C^{19}H_3$); 1.11 s and 1.14 s (3H, $C^{21}H_3$, $C^{21'}H_3$); 1.28 s, 1.38 s, 1.40 s, and 1.50 s (3H each, Me_2C); 1.78–2.20 m (13H, CH, CH_2); 1.62 s (~2.7H, $C^{26'}H_3$); 1.70 s and 1.72 s (3H, $C^{27}H_3$, $C^{27'}H_3$); 2.22 m (1H, 7α-H); 2.30 m (1H, 17-H); 2.37 m (1H, 8-H); 2.57 br.s (1H, 5-H, $w_{1/2}$ = 10.7 Hz); 2.70 t (1H, 7β-H, J = 13.4 Hz); 3.65–3.71 m (1H, 22-H, 22′-H); 4.20 m (1H, 2-H, $w_{1/2}$ = 13.0 Hz); 4.49 m (1H, 3-H, $w_{1/2}$ = 22.6 Hz); 4.69 br.s and 4.72 br.s (1.3H, 26-H, $w_{1/2}$ = 6.8 Hz); 5.17 t (0.7H, 24′-H, J = 6.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.9 q (C^{18}), 18.2 t (C^{11}), 18.6 q ($C^{27'}$), 21.1 t (C^{16}), 21.4 q (C^{21}), 22.5 q (C^{27}), 25.4 t (C^{23}), 25.7 q (C^{19}), 25.9 q ($C^{26'}$), 26.0 q and 28.5 q (2,3-**Me**$_2$C), 26.8 q and 29.6 q (20,22-**Me**$_2$C), 27.7 t (C^4), 31.5 t (C^{15}), 33.3 t (C^{12}), 34.4 t (C^{24}), 35.0 t (C^1), 39.6 s (C^{10}), 41.3 t (C^7), 41.6 d and 41.7 d (C^9), 43.8 d and 43.9 d (C^8), 46.9 s (C^{13}), 50.0 d and 50.1 d (C^{17}), 50.6 d (C^5), 70.9 d (C^3), 73.5 d (C^2), 80.6 d and 81.0 d (C^{22}), 84.1 s (C^{20}), 85.0 s (C^{14}), 106.7 s and 106.8 s (20,22-Me$_2$**C**), 107.6 s (2,3-Me$_2$**C**), 110.0 t (C^{26}), 120.4 d ($C^{24'}$), 133.5 q ($C^{25'}$), 145.3 s (C^{25}), 211.9 s (C^6).

(20*R*,22*R*)-2β,3β:20,22-Bis(isopropylidenedioxy)-5α-cholesta-7,14-diene-6β,25-diol (IX). Diacetonide **II**, 1 g (1.79 mmol), was dissolved in 50 ml of anhydrous THF, 0.198 g (5.37 mmol) of $LiAlH_4$ was added, and the mixture was stirred for 1 h at ~25°C under argon. The mixture was cooled to 0°C, 5 ml of water was added, and ~7 ml of 5% hydrochloric acid was added to a weakly acidic reaction. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×70 ml). The extracts were combined with the organic phase and evaporated under reduced pressure, and the residue was subjected to chromatography on 40 g of silica gel using chloroform as eluent to isolate 0.1 g (10%) of dienol **IX**, R_f 0.7 ($CHCl_3$–MeOH, 10:1), 0.3 g (30%) of **V**, R_f 0.63 ($CHCl_3$–MeOH, 10:1), and 0.53 g (53%) of **VII**.

Dienol (**IX**). mp 90–92°C, $[\alpha]_D^{19}$ = –62.8° (c = 7.32, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.01 s (3H, $C^{18}H_3$); 1.04 s (3H, $C^{19}H_3$); 1.18 s (3H, $C^{21}H_3$); 1.22 s (6H, $C^{26}H_3$, $C^{27}H_3$); 1.29 s, 1.31 s, 1.41 s, and 1.50 s (3H each, Me_2C); 1.52–2.58 m (15H, CH, CH_2); 3.72 m (1H, 22-H, $w_{1/2}$ = 15.3 Hz); 3.81 m (1H, 6-H, $w_{1/2}$ = 10 Hz); 4.05 m (1H, 2-H, $w_{1/2}$ = 20 Hz); 4.19 m (1H, 3-H, $w_{1/2}$ = 11 Hz); 5.62 br.s (1H, 15-H, $w_{1/2}$ = 8 Hz); 5.89 br.s (1H, 7-H, $w_{1/2}$ = 9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 18.4 q (C^{18}), 20.9 t (C^{11}), 21.1 q (C^{21}), 23.7 t (C^{23}), 24.8 q (C^{19}), 28.3 t (C^4), 29.0 q (C^{27}), 29.6 q (C^{26}), 26.5 q and 28.6 q (2,3-**Me**$_2$C), 26.8 q and 28.8 q (20,22-**Me**$_2$C), 30.9 t (C^{12}), 34.3 s (C^{10}), 37.2 d (C^9), 39.2 t (C^{16}), 40.4 t (C^{24}), 41.2 t (C^1), 43.3 d (C^5), 47.3 s (C^{13}), 57.6 d (C^{17}), 70.3 s (C^{25}), 70.8 d (C^6), 72.3 d (C^2), 72.8 d (C^3), 81.7 d (C^{22}), 83.6 s (C^{20}), 106.8 s (20,22-Me$_2$**C**), 107.9 s (2,3-Me$_2$**C**), 120.3 d (C^{15}), 121.2 d (C^7), 135.2 s (C^{14}), 150.0 s (C^8).

(20*R*,22*R*)-2β,3β:20,22-Bis(isopropylidenedioxy)-5β,8α-cholest-14-ene-6β,25-diol (X). Diacetonide **II**, 0.3 g (0.54 mmol), was dissolved in 20 ml of anhydrous THF, 0.1 g (2.70 mmol) of $LiAlH_4$ was added, and the mixture was stirred for 1 h at ~25°C under argon. The mixture was cooled to 0°C, 5 ml of water was added, and ~5 ml of 5% hydrochloric acid was added to a weakly acidic reaction. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate (3×50 ml). The extracts were combined with the organic phase and evaporated under reduced pressure, and the residue was subjected to chromatography on 20 g of silica gel using chloroform as eluent to isolate 0.05 g (17%) of diol **X**, R_f 0.69 ($CHCl_3$–MeOH, 10:1), 0.088 g (30%) of **V**, R_f 0.63 ($CHCl_3$–MeOH, 10:1), and 0.15 g (50%) of **VII**.

Diol (**X**). mp 75–77°C, $[\alpha]_D^{24}$ = +35.6° (*c* = 2.74, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.13 s (3H, $C^{18}H_3$); 1.16 s (3H, $C^{19}H_3$); 1.18 s (3H, $C^{21}H_3$); 1.22 s (6H, $C^{26}H_3$, $C^{27}H_3$); 1.30 s, 1.41 s, and 1.51 s (2:1:1, 12H, Me_2C); 1.60–2.52 m (20H, CH, CH_2); 3.07 m (1H, 8-H); 3.75 m (1H, 22-H, $w_{1/2}$ = 21 Hz); 3.95 br.s (1H, 6-H, $w_{1/2}$ = 12 Hz); 4.36 m (1H, 2-H, $w_{1/2}$ = 13 Hz); 4.63 m (1H, 3-H, $w_{1/2}$ = 16 Hz); 5.35 br.s (1H, 15-H, $w_{1/2}$ = 13 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.7 t (C^{11}), 20.8 q (C^{18}), 23.7 t (C^{23}), 25.8 q (C^{21}), 26.7 q and 28.9 q (2,3-**Me**$_2$C), 27.3 q and 28.9 q (20,22-**Me**$_2$C), 28.6 q (C^{19}), 29.7 q (C^{26}, C^{27}), 30.5 t (C^{16}), 31.0 d (C^9), 31.6 t (C^4), 33.4 t (C^{10}), 36.0 t (C^7), 37.9 t (C^1), 41.0 d (C^5), 41.4 s (C^{12}), 43.1 t (C^{24}), 46.8 s (C^{13}),48.2 d (C^8), 59.5 d (C^{17}), 70.3 s (C^{25}), 71.6 d (C^6), 72.7 d (C^3), 74.6 d (C^2), 81.8 d (C^{22}), 83.7 s (C^{20}), 106.7 s (20,22-Me_2**C**), 107.0 s (2,3-Me_2**C**), 120.6 d (C^{15}), 154.4 s (C^{14}).

(20*R*,22*R*)-2β,3β:20,22-Bis(isopropylidenedioxy)-5β,8α-cholestane-6α,14α,25-triol (XI). Diacetonide **V**, 0.18 g (0.32 mmol), was dissolved in 7 ml of anhydrous THF, 0.025 g (0.64 mmol) of $LiAlH_4$ was added, and the mixture was stirred for 0.5 h at ~25°C under argon. The mixture was cooled to 0°C, 5 ml of water was added, and ~7 ml of 5% hydrochloric acid was added to a weakly acidic reaction. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3×40 ml). The extracts were combined with the organic phase and evaporated under reduced pressure, and the residue was subjected to chromatography on 8 g of silica gel using chloroform as eluent. Yield 0.16 g (90%), R_f 0.34 ($CHCl_3$–MeOH, 10:1), mp 137–139°C, $[\alpha]_D^{20}$ = +25.7° (*c* = 9.33, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 1.00 s (3H, $C^{18}H_3$); 1.08 s (3H, $C^{21}H_3$); 1.18 s (9H, $C^{19}H_3$, $C^{26}H_3$, $C^{27}H_3$); 1.27 s, 1.37 s, and 1.47 s (2:1:1, 12H, Me_2C); 1.60–2.00 m (20H, CH, CH_2); 2.13 m (1H, 17-H, $w_{1/2}$ = 19 Hz); 2.32 m (1H, 8-H, $w_{1/2}$ = 24 Hz); 3.62 m (1H, 22-H, $w_{1/2}$ = 16 Hz); 3.94 br.s (1H, 6-H, $w_{1/2}$ = 10 Hz); 4.29 m (1H, 2-H, $w_{1/2}$ = 12 Hz); 4.58 m (1H, 3-H, $w_{1/2}$ = 16 Hz); in DMSO-d_6 (500.13 MHz): 0.92 s (3H, $C^{18}H_3$), 1.01 s (3H, $C^{21}H_3$), 1.06 s ($C^{27}H_3$), 1.07 s (6H, $C^{19}H_3$, $C^{26}H_3$), 1.18 s and 1.37 s (6H, 2,3-Me_2C), 1.22 s and 1.31 s (6H, 20,22-Me_2C), 1.15 m and 1.79 m (2H, 15-H), 1.30 m and 2.33 m (2H, 1-H), 1.34 m and 1.37 m (2H, 23-H), 1.31 m and 1.54 m (2H, 24-H), 1.35 m and 1.39 m (2H, 11-H), 1.51 m and 1.71 m (2H, 12-H), 1.46 m and 1.71 m (2H, 7-H), 1.63 m and 1.68 m (2H, 4-H), 1.37 m (1H, 5-H), 1.66 m and 1.79 m (2H, 16-H), 1.81 m (1H, 9-H), 2.20 m (1H, 17-H), 2.31 m (1H, 8-H), 3.56 m (1H, 22-H), 3.65 s (1H, 14-OH), 3.75 m (1H, 6-H), 4.13 s (1H, 25-OH), 4.19 m (1H, 2-H), 4.39 d (1H, 6-OH, *J* = 3.5 Hz), 4.51 m (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: in $CDCl_3$: 18.0 t (C^{11}); 18.3 q (C^{18}); 21.4 t (C^{16}); 23.5 t (C^{23}); 25.9 q (C^{21}); 26.7 q (C^{19}); 27.6 q, 28.6 q, 28.8 q, and 28.9 q (**Me**$_2$C); 29.6 q (C^{26}, C^{27}); 31.2 t (C^{15}); 31.5 t (C^4); 33.4 s (C^7, C^{10}); 34.0 t (C^{12}); 36.5 t (C^1); 36.7 d (C^8); 41.3 t (C^{24}); 42.3 d (C^5, C^9); 46.6 s (C^{13}); 49.8 d (C^{17}); 70.2 s (C^{25}); 71.8 d (C^6); 72.6 d (C^3); 74.6 s (C^2); 81.8 d (C^{22}); 84.6 s (C^{14}); 86.1 s (C^{20}); 106.7 s (20,22-Me_2**C**); 107.0 s (2,3-Me_2**C**); in DMSO (500.13 MHz): 17.9 t (C^{11}), 18.1 q (C^{18}), 21.2 t (C^{16}), 21.4 q (C^{21}), 23.2 t (C^{23}), 25.9 q and 28.6 q (2,3-**Me**$_2$C), 26.7 q and 29.0 q (20,22-**Me**$_2$C), 27.3 q (C^{19}), 29.0 q (C^{27}), 29.6 q (C^{26}), 30.4 t (C^{15}), 31.7 t (C^4), 32.8 s (C^7), 33.0 s (C^{10}), 33.6 t (C^{12}), 35.9 d (C^8), 36.2 t (C^1), 41.1 t (C^{24}), 41.2 d (C^5), 41.5 d (C^9), 46.1 s (C^{13}), 49.3 d (C^{17}), 68.4 s (C^{25}), 70.3 d (C^6), 71.9 d (C^3), 74.2 s (C^2), 81.3 d (C^{22}), 83.9 s (C^{14}), 84.3 s (C^{20}), 105.8 s (20,22-Me_2**C**), 106.0 s (2,3-Me_2**C**).

(20*R*,22*R*)-2β,3β,14α,25-Tetrahydroxy-20,22-isopropylidenedioxy-5β,8α-cholestan-6-one (XII, 7,8α-dihydro-20-hydroxyecdysone 20,22-acetonide (XII). A mixture of 0.22 g (0.46 mmol) of compound **V** and 3 ml of glacial acetic acid was stirred for 5.5 h. The mixture was evaporated, and the residue was subjected to chromatography on 9 g of silica gel using chloroform–methanol (20:1) as eluent. Yield 0.1 g (49%), R_f 0.60 ($CHCl_3$–MeOH, 5:1), mp 134–136°C, $[\alpha]_D^{18}$ = +7.2° (*c* = 8.67, $CHCl_3$). IR spectrum: ν(C=O) 1700 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.06 s (3H, $C^{18}H_3$), 1.11 s (3H, $C^{21}H_3$), 1.21 s (6H, $C^{26}H_3$, $C^{27}H_3$), 1.29 s (3H, $C^{19}H_3$), 1.39 s (6H, Me_2C), 1.42–2.10 m (19H, CH, CH_2), 2.31 t (1H, 8-H, *J* = 12.5 Hz), 2.43 m

(1H, 5-H, $w_{1/2}$ = 11 Hz), 2.67 t (1H, 7β-H, J = 14.5 Hz), 3.63 m (1H, 22-H, $w_{1/2}$ = 15 Hz), 3.84 m (1H, 2-H, $w_{1/2}$ = 18 Hz), 3.93 m (1H, 3-H, $w_{1/2}$ = 12 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 18.4 q (C^{18}), 20.1 t (C^{11}), 21.1 t (C^{16}), 21.4 q (C^{21}), 23.4 t (C^{23}), 25.0 t (C^4), 26.7 q (C^{19}), 26.9 q and 28.9 q (20,22-**Me**$_2$C), 29.1 q (C^{27}), 29.4 q (C^{26}), 31.3 t (C^{15}), 33.5 t (C^{12}, C^1), 39.4 s (C^{10}), 41.0 d (C^9), 41.1 t (C^7), 41.3 t (C^{24}), 43.0 d (C^8), 46.8 s (C^{13}), 49.8 d (C^{17}), 51.1 d (C^5), 70.4 s (C^{25}), 66.7 d (C^3), 69.5 d (C^2), 81.9 d (C^{22}), 84.4 s (C^{20}), 85.0 s (C^{14}), 106.8 s (20,22-Me$_2$**C**), 212.8 s (C^6).

(20*R*,22*R*)-2β,3β,25-Trihydroxy-20,22-isopropylidenedioxy-5β,8α-cholest-14-en-6-one (XIII, 7,8α-dihydrostachysterone B 20,22-acetonide). A mixture of 0.125 g (0.22 mmol) of compound **V** and 3 ml of 70% acetic acid was stirred for 1.5 h, 0.045 g (0.33 mmol) of $ZnCl_2$ was added, and the mixture was stirred for 2.5 h until the reaction was complete (TLC). The mixture was diluted with 30 ml of water and extracted with butanol (3×20 ml), the extracts were combined and evaporated under reduced pressure, and the residue was subjected to chromatography on 8 g of silica gel using chloroform–methanol (20:1) as eluent. Yield 0.067 g (60%), R_f 0.47 ($CHCl_3$–MeOH, 20:1), mp 118–120°C, $[\alpha]_D^{24}$ = –123° (c = 1.18, $CHCl_3$). IR spectrum: ν(C=O) 1700 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 s (6H, $C^{18}H_3$, $C^{21}H_3$), 1.21 s (6H, $C^{26}H_3$, $C^{27}H_3$), 1.28 s (3H, $C^{19}H_3$), 1.40 s and 1.41 s (3H each, Me_2C), 1.46–2.21 m (15H, CH, CH_2), 2.15 d.d (1H, 7α-H, J = 14.5, 4.4 Hz), 2.36 m (1H, 5-H, $w_{1/2}$ = 10 Hz), 2.48 d.d (1H, 17-H, J = 14.5, 11.0 Hz), 2.73 t (1H, 7β-H, J = 14.5 Hz), 3.03 d.t (1H, 8-H, J = 14.5, 4.0 Hz), 3.72 m (1H, 22-H, $w_{1/2}$ = 5 Hz), 3.87 m (1H, 2-H, $w_{1/2}$ = 24 Hz), 3.97 m (1H, 3-H, $w_{1/2}$ = 11 Hz), 5.33 m (1H, 15-H, $w_{1/2}$ = 8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.9 t (C^{11}), 21.0 q (C^{18}, C^{21}), 23.6 t (C^{23}), 24.3 t (C^{16}), 26.7 q (C^{19}), 28.8 q (20,22-**Me**$_2$C), 29.0 q (C^{26}), 29.5 q (C^{27}), 30.4 t (C^4), 37.3 d (C^9), 38.4 t (C^1), 39.8 s (C^{10}), 41.2 t (C^{24}), 42.4 t (C^{12}), 44.2 t (C^7), 46.7 s (C^{13}), 47.3 d (C^8), 51.2 d (C^5), 59.3 d (C^{17}), 70.3 s (C^{25}), 66.7 d (C^3), 69.5 d (C^2), 81.6 d (C^{22}), 83.4 s (C^{20}), 106.8 s (20,22-Me$_2$**C**), 122.2 d (C^{15}), 151.1 s (C^{14}), 211.9 s (C^6).

(20*R*,22*R*)-2β,3β,20,22,25-Pentahydroxy-5β,8α-cholest-14-en-6-one (XIV, 7,8α-dihydrostachysterone B). Compound **V**, 0.2 g (0.36 mmol), was dissolved in 3.6 ml of methanol, 1 ml of 10% perchloric acid was added, the mixture was stirred for 3.5 h and cooled to 5°C, 2 ml of water and 1 ml of a saturated solution of $NaHCO_3$ were added, and the mixture was extracted with ethyl acetate (3×20 ml). The extracts were combined and evaporated under reduced pressure, and the residue was subjected to chromatography on 8 g of silica gel using chloroform–methanol (20:1) as eluent. Yield 0.07 g (33%), R_f 0.38 ($CHCl_3$–MeOH, 5:1), mp 112–114°C, $[\alpha]_D^{18}$ = –56.3° (c = 1.1, MeOH). IR spectrum: ν(C=O) 1700 cm^{-1}. ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.17 s (3H, $C^{18}H_3$), 1.19 s (3H, $C^{19}H_3$), 1.20 s (3H, $C^{21}H_3$), 1.26 s (3H, $C^{26}H_3$), 1.42 s (3H, $C^{27}H_3$), 1.50–2.40 m (17H, CH, CH_2), 2.48 m (1H, 5-H, $w_{1/2}$ = 11 Hz), 2.88 t (1H, 7β-H, J = 14 Hz), 3.07 m (1H, 8-H, $w_{1/2}$ = 25 Hz), 3.30 m (1H, 22-H), 3.74 m (1H, 2-H, $w_{1/2}$ = 19 Hz), 3.92 m (1H, 3-H, $w_{1/2}$ = 10 Hz), 5.39 br.s (1H, 15-H, $w_{1/2}$ = 8 Hz). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 19.2 t (C^{11}), 20.1 q (C^{21}), 21.9 q (C^{18}), 25.3 t (C^{23}), 27.3 t (C^{16}), 27.5 q (C^{19}), 28.9 q (C^{26}), 29.4 q (C^{27}), 30.7 t (C^4), 38.9 d (C^9), 40.3 t (C^1), 41.0 s (C^{10}), 42.3 t (C^{12}, S^{24}), 44.5 t (C^7), 45.4 d (C^8), 52.4 d (C^5), 60.8 d (C^{17}), 71.3 s (C^{25}), 68.1 d (C^3), 71.0 d (C^2), 77.2 s (C^{20}), 78.6 d (C^{22}), 123.7 d (C^{15}), 152.9 s (C^{14}), 214.0 s (C^6); the C^{13} signal was obscured by the solvent.

(20*R*,22*R*)-2β,3β-Dihydroxy-20,22-isopropylidenedioxy-5β,8α-cholest-14-en-6-one (XV). Hydrogen was passed through a suspension of 0.26 g (0.48 mmol) of compound **VI** and 0.1 g (10%) of Pd/C in 5 ml of ethanol under stirring at at ~25°C. After 3 days, the mixture was filtered, the catalyst was washed with ethanol, and the filtrate was evaporated under reduced pressure. The residue was subjected to chromatography on 6 g of silica gel using chloroform as eluent. Yield 0.094 g (41%), R_f 0.39 ($CHCl_3$–MeOH, 20:1), mp 110–112°C, $[\alpha]_D^{23}$ = –18.6° (c = 11.15, $CHCl_3$). IR spectrum: ν(C=O) 1710 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 d (6H, $C^{26}H_3$, $C^{27}H_3$, J = 6.5 Hz), 1.14 s (3H, $C^{21}H_3$), 1.17 s (3H, $C^{18}H_3$), 1.27 s (3H, $C^{19}H_3$), 1.40 s and 1.42 s (6H, Me_2C), 1.46–2.22 m (16H, CH, CH_2), 2.15 d.d (1H, 7α-H, J = 14.5, 3.4 Hz), 2.37 m (1H, 9-H, $w_{1/2}$ = 11 Hz), 2.49 d.d (1H, 5-H, J = 11.7, 14.8 Hz), 2.74 t (1H, 7β-H, J = 14.5 Hz), 3.04 d.t (1H, 8-H, J = 13.8, 5.1 Hz), 3.69 d.d (1H, 22-H, J = 8.6, 2.5 Hz), 3.91 m (1H, 3-H, $w_{1/2}$ = 24 Hz), 3.99 m (1H, 2-H, $w_{1/2}$ = 11 Hz), 5.35 m (1H, 15-H, $w_{1/2}$ = 6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.9 t (C^{11}), 21.0 q (C^{18}), 21.0 q (C^{21}), 22.4 q (C^{26}), 22.4 q (C^{27}), 24.3 t (C^{23}), 26.7 q (C^{19}), 26.8 t (C^{16}), 28.9 s (C^{25}), 28.1 q and 28.9 q (20,22-**Me**$_2$C), 30.4 t (C^4), 36.2 t (C^{24}), 37.4 d (C^9), 38.3 t (C^1), 39.8 s (C^{10}), 42.5 t (C^{12}), 44.2 t (C^7), 46.8 s (C^{13}), 47.3 d (C^8),

51.2 d (C^5), 59.5 d (C^{17}), 69.6 d (C^3), 70.7 d (C^2), 81.3 d (C^{22}), 83.2 s (C^{20}), 106.6 s (20,22-Me_2**C**), 122.3 d (C^{15}), 151.1 s (C^{14}), 212.0 s (C^6).

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