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Transformation of 20-Hydroxyecdysone Acetonides into Podecdysone B

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Abstract—Hydrogenation of 20-hydroxyecdysone 2,3:20,22-diacetonide and 20,22-acetonide over palladium catalyst yields podecdysone B 20,22-acetonide. Acid hydrolysis of the latter affords podecdysone B which is a natural phytoecdysteroid.

Ecdysteroids are widely spread in animals; they act as moulting and metamorphosis hormones of Anthropoda species [1]. The concentration of zooecdysteroids in animals is extremely low, whereas in some plants the concentration of phytoecdysteroids reaches 1.5–2% [2]. One of the most accessible phytoecdysteroids is 20-hydroxyecdysone; it was used as starting compound in the synthesis of a number of phyto- and zooecdysteroids [3–5].

While studying chemical transformations of 20-hydroxyecdysone, we have found that 2,3:20,22-diacetonide **I** and 20,22-acetonide **II** derived therefrom are converted into podecdysone B 20,22-acetonide (**III**) by hydrogenation over palladium catalyst (10% Pd/C) in chloroform. In both cases, the product was an equimolar mixture of compounds **II** and **III**. Analogous results were obtained when the reaction was carried out in methylene chloride and carbon tetrachloride, whereas no reaction occurred in other solvents (such as isobutyl alcohol or ethanol). Compounds **I** and **II** did not undergo any transformations over Pd/C in the absence of hydrogen.

The product mixture containing compounds **II** and **III** was separated by column chromatography. The structure of **III** follows from its spectral parameters. The absorption maximum in the UV spectrum of acetonide **III** is located at λ 244 nm (ε = 13200), indicating the presence of a conjugated diene system which is typical of podecdysone [6]. In the IR spectrum we observed characteristic absorption bands at 1650 (C=CC=C), 1710 (C=O), and 3400 cm^{-1} (OH). The signal from the carbonyl carbon atom in the ^{13}C NMR spectrum of **III** is displaced downfield ($\Delta\delta_C$ 10 ppm) relative to the corresponding signal of initial compounds **I** and **II** due to the lack of conjugation between the carbonyl group and the double bond. sp^2-Hybridized carbon atoms of the conjugated diene system give rise to the following signals, δ_C, ppm: 122.2 (C^8), 135.5 (C^9), 148.0 (C^{14}), and 119.0 (C^{15}). In the acetal region, only one carbon signal was present at δ_C 106.9 ppm, indicating that the 20,22-acetonide moiety remains unchanged during the reaction; the 2,3-acetonide fragment in diacetonide **I** (δ 108.2 ppm) undergoes hydrogenation. The ^1H NMR spectrum of **III** contained an olefinic proton signal at δ 5.36 ppm (15-H) instead of the 7-H signal from the initial compound (δ 6.07 ppm).

Acid hydrolysis (70% AcOH–$ZnCl_2$) of acetonide **III** afforded podecdysone **B** (**IV**) which is a natural phytoecdysteroid isolated from plants [6, 7]. Compound **IV** was also synthesized in a low yield by acid dehydration of 20-hydroxyecdysone and by enzymatic hydrolysis of podecdysone B 25-*O*-β-D-glucopyranoside isolated from *Pfaffia iresinoides* roots [8].

Monitoring of the transformation of diacetonide **I** by thin-layer chromatography showed that the initial compound is converted first into acetonide **II** via removal of relatively labile 2,3-acetonide group. The subsequent transformations are similar for the two compounds (**I** and **II**). As a result, a 1:1 mixture of **II** and **III** is obtained. Our attempts to increase the

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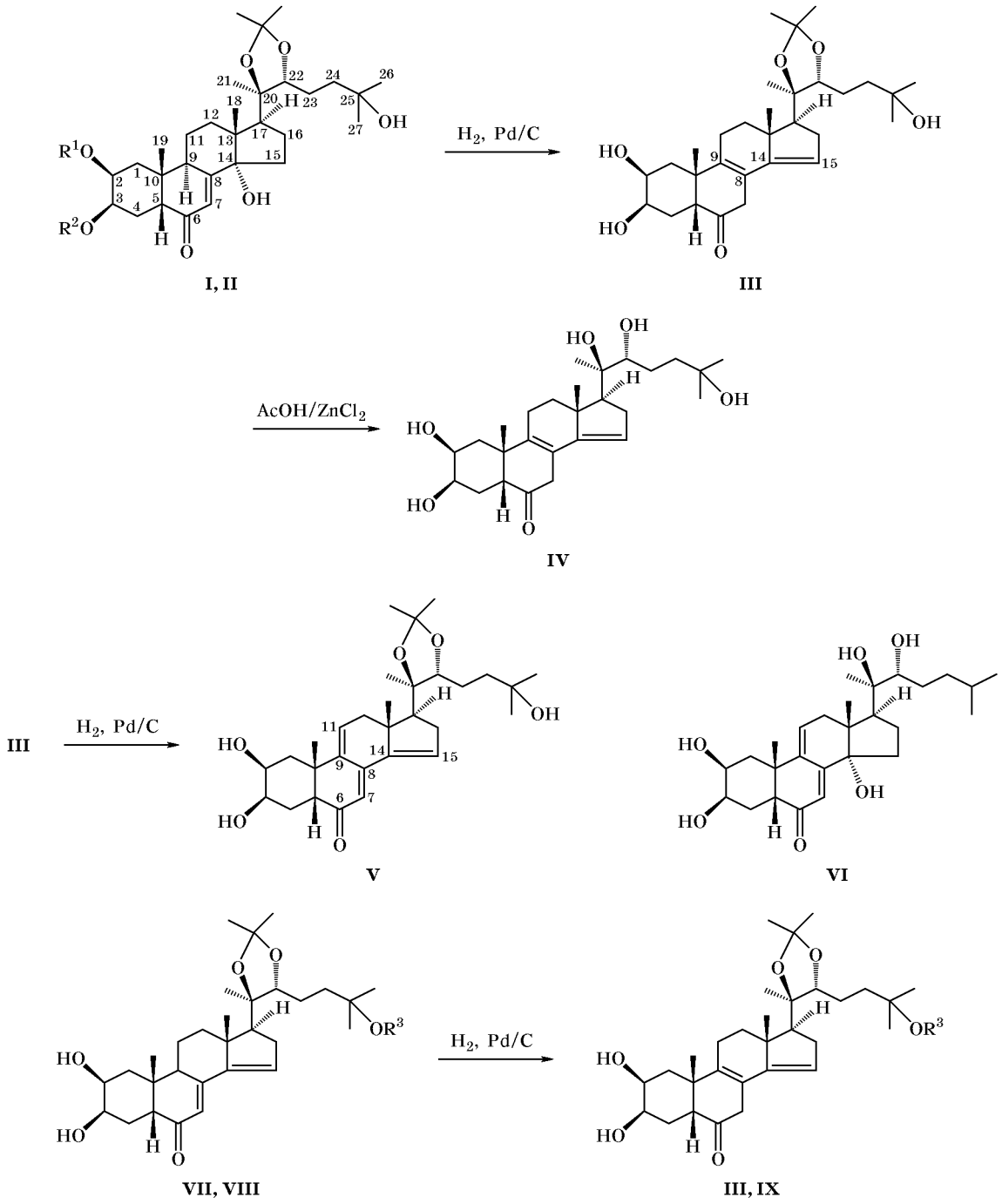
Scheme 1.



I, $R^1R^2 = Me_2C$; **II**, $R^1 = R^2 = H$; **VII**, $R^3 = H$; **VIII**, **IX**, $R^3 = COCF_3$.

conversion of **II** into **III** by prolonging the reaction led to formation of a complex mixture of by-products.

Under analogous conditions, compound **III** was converted into trienone **V**. The latter was isolated by column chromatography from a 1:1 mixture with **III**. Compound **V** is 14,15-anhydro-25-hydroxydacryhainansterone 20,22-acetonide (dacryhainansterone has structure **VI** [1, 6]). Acetonide **V** characteristically showed in the ^{13}C NMR spectrum downfield signals at δ_C 203.85 (C^6), 145.45 (C^9), 143.83 (C^8), 135.23 (C^{14}), 131.78 (C^{11}), 128.92 (C^{15}), and 116.29 ppm (C^7), which belong to the oxotriene system.

In keeping with published data [9], the transformation of enone **II** into dienone **III** may be presumed to involve intermediate formation of 14,15-anhydro derivative **VII**. This compound (stachysterone B 20,22-acetonide) was obtained by us previously from acetonide **II** [10]. However, conjugated diene **VII** was not detected by TLC in the reaction mixture throughout the transformation of **II** into **III**. Our results are consistent with the data of Galbraith and Horn [11], according to which acid treatment of 20-hydroxyecdysone is not accompanied by dehydration of the allylic hydroxy group at C^{14}. On the other hand, compound **VII** and its 25-*O*-trifluoroacetyl derivative **VIII** (which was synthesized as described in [10]) undergo isomerization into compounds **III** and **IX**, respectively. Hence we can conclude that in the transformation of acetonides **I** and **II** into **III** the dehydration and isomerization processes occur in a concerted fashion.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR75 spectrometer from samples pelleted with KBr. The UV spectra were measured on a Specord M-40 spectrophotometer using CH_3OH and $CHCl_3$ as solvents. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-300 instrument operating at 300.13 (^1H) and 75 MHz (^{13}C); $CDCl_3$, CD_3OD, and C_5D_5N were used as solvents; the chemical shifts were measured relative to TMS as internal reference. The melting points were determined on a compact Boetius device. The specific rotations were measured using a Perkin–Elmer 141 polarimeter. Thin-layer chromatography was performed on Silufol plates; spots were visualized by treatment with a solution of 4-hydroxy-3-methoxybenzaldehyde in ethanol acidified with sulfuric acid.

Podecdysone B 20,22-acetonide or (20*R*,22*R*)-20,22-*O*-isopropylidene-2β,3β,25-trihydroxy-5β-cholesta-8,14-dien-6-one (III). *a*. Diacetonide **I** was prepared by the procedure reported in [10] from 20-hydroxyecdysone isolated from *Serratula coronata* [12]; mp 234–235°C, $[\alpha]_D^{15}$ = +39.4° (*c* = 1.1, $CHCl_3$); ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.9 q (C^{18}), 20.4 t (C^{11}), 21.1 t (C^{16}), 21.8 q (C^{21}), 23.4 q (C^{19}), 23.5 t (C^{23}), 26.5 t (C^{15}), 26.5 q (C^{26}), 26.8 q (C^{27}), 28.4 q and 28.4 q (20,22-**Me**$_2$$CO_2$), 28.9 q and 29.3 q (2,3-**Me**$_2$$CO_2$), 30.8 t ($C^{12}$), 31.3 t ($C^4$), 34.3 d ($C^9$), 37.5 t ($C^1$), 37.7 s ($C^{10}$), 41.3 t ($C^{24}$), 47.2 s ($C^{13}$), 48.9 d ($C^{17}$), 50.7 d ($C^5$), 70.3 s ($C^{25}$), 71.5 d ($C^3$), 72.0 d ($C^2$), 81.9 d ($C^{22}$), 84.3 s ($C^{20}$), 84.7 s ($C^{14}$), 106.9 s (20,22-Me$_2$**C**$O_2$), 108.2 s (2,3-Me$_2$**C**$O_2$), 121.2 d ($C^7$), 163.7 s ($C^8$), 203.0 s ($C^6$). A mixture of 0.5 g (0.89 mmol) of diacetonide **I**, 0.05 g of the catalyst (10% Pd/C), and 5 ml of chloroform, methylene chloride, or carbon tetrachloride was stirred at room temperature under hydrogen until the conversion of initial compound **I** was complete and the conversion of intermediate product **II** was about 50% (~7 days, TLC monitoring). The mixture was evaporated, and the residue (~2 ml) was subjected to chromatography in a column charged with 20 g of silica gel (eluent $CHCl_3$–MeOH, 7 : 1) to isolate 0.22 g (48%) of product **II** and 0.22 g (49%) of **III**.

Compound **II**. R_f 0.4. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 17.1 q (C^{18}), 20.8 t (C^{11}), 21.9 t (C^{16}), 22.2 q (C^{21}), 24.1 t (C^{23}), 24.2 q (C^{19}), 29.3 q (C^{26}), 29.3 q (C^{27}), 29.7 q and 29.9 q (20,22-**Me**$_2$$CO_2$), 31.4 t ($C^{12}$), 31.5 t ($C^{15}$), 32.2 t ($C^4$), 34.2 d ($C^9$), 37.7 t ($C^1$), 38.4 s ($C^{10}$), 41.9 t ($C^{24}$), 47.6 s ($C^{13}$), 49.7 d ($C^{17}$), 51.1 d ($C^5$), 67.8 d ($C^3$), 67.9 d ($C^2$), 69.1 s ($C^{25}$), 82.3 d ($C^{22}$), 83.9 s ($C^{20}$), 85.1 s ($C^{14}$), 106.7 s (20,22-Me$_2$**C**$O_2$), 121.5 d ($C^7$), 165.4 s ($C^8$), 203.3 s ($C^6$).

Compound **III**. R_f 0.6; mp 120–122°C, $[\alpha]_D^{18}$ = –58.3° (*c* = 0.4, MeOH). IR spectrum (KBr), ν, cm^{-1}: 1650, 1710, 3400. UV spectrum, λ_{max}, nm: 244 (ε = 12 310). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.93 s (3H, 19-H); 0.99 s (3H, 18-H); 1.17 s (3H, 21-H); 1.19 s and 1.21 s (6H, 26-H, 27-H); 1.27 s and 1.38 s (6H, 20,22-Me$_2$$CO_2$); 0.70–2.74 m (18H, CH, CH_2), 3.46 d.d (1H, 22-H, ^3J = 11.7, 2.1); 3.64 m (1H, 2-H, $w_{1/2}$ = 17); 3.95 m (1H, 3-H, $w_{1/2}$ = 6); 5.33 m (1H, 15-H, $w_{1/2}$ = 4). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.4 q (C^{18}), 21.2 t (C^{11}), 21.2 q (C^{21}), 23.7 t (C^{23}), 26.8 q (C^{19}), 28.9 q (C^{26}), 29.1 q (C^{27}), 29.5 t (C^{16}), 29.5 q and 29.7 q (20,22-**Me**$_2$$CO_2$), 31.5 t ($C^4$), 36.5 t ($C^7$), 37.3 t ($C^{24}$), 38.6 t ($C^{12}$), 41.2 t ($C^1$), 43.0 s ($C^{10}$), 45.8 s ($C^{13}$), 52.2 d ($C^5$), 56.0 d ($C^{17}$), 67.4 d ($C^3$), 68.9 d ($C^2$), 70.4 s ($C^{25}$), 81.8 d ($C^{22}$), 83.0 s ($C^{20}$), 106.9 s (20,22-Me$_2$**C**$O_2$), 119.0 d ($C^{15}$), 122.2 s ($C^8$), 135.5 s ($C^9$), 148.0 s ($C^{14}$), 213.2 s ($C^6$). Found, %: C 71.96; H 9.36. $C_{30}H_{46}O_6$. Calculated, %: C 71.68; H 9.22.

b. A mixture of 0.5 g (0.96 mmol) of acetonide **II** {mp 223–224°C, $[\alpha]_D^{18}$ = +58.5° (*c* = 0.9, $CHCl_3$); prepared by the procedure reported in [10] from 20-hydroxyecdysone}, 0.05 g of 10% Pd/C), and 5 ml of chloroform was stirred at room temperature under hydrogen until the conversion of **II** reached 50% (~7 days, TLC). The mixture was evaporated, and the residue (~2 ml) was subjected to column chromatog-

raphy on 20 g of silica gel (eluent $CHCl_3$–MeOH, 7:1) to isolate 0.24 g (49%) of initial compound **II** (R_f 0.4) and 0.23 g (48%) of **III** (R_f 0.6). Product **III** was identical in the melting point, $[\alpha]_D$ value, and ^1H and ^{13}C NMR spectra to a sample prepared as described in *a*.

c. Compound **VII** was synthesized by the procedure described in [10]; mp 124–125°C, $[\alpha]_D^{17}$ = –9.0° (*c* = 0.7, MeOH); ^{13}C NMR spectrum* (CD_3OD), δ_C, ppm: 19.9 q (C^{18}), 22.3 t (C^{11}), 24.1 q (C^{19}), 24.1 q (C^{21}), 25.1 t (C^{23}), 27.3 t (C^{12}), 29.0 q (C^{26}), 29.3 q (C^{27}), 29.3 q and 29.7 q (20,22-**Me**$_2$$CO_2$), 32.8 t ($C^4$), 36.9 t ($C^{16}$), 39.4 t ($C^1$), 39.8 d ($C^9$), 40.0 s ($C^{10}$), 42.0 t ($C^{24}$), 51.5 d ($C^5$), 58.8 d ($C^{17}$), 68.6 d ($C^2$), 68.6 d ($C^3$), 71.3 s ($C^{25}$), 83.1 d ($C^{22}$), 84.8 s ($C^{20}$), 108.2 s (20,22-Me$_2$**C**$O_2$), 121.1 d ($C^7$), 130.2 d ($C^{15}$), 158.9 s ($C^8$), 150.4 s ($C^{14}$), 206.1 s ($C^6$). Following the procedure described above in *b*, from 0.2 g (0.4 mmol) of compound **VIIc** we obtained (after chromatographic separation in a column charged with 8 g of silica gel, eluent $CHCl_3$–MeOH, 7:1) 98 mg (49%) of initial compound **VII** (R_f 0.5) and 94 mg (47%) of compound **III** (R_f 0.6) which was identical to a sample prepared as described in *a*.

Podecdysone B or (20*R*,22*R*)-2β,3β,20,22,25-pentahydroxy-5β-cholesta-8,14-dien-6-one (IV). A mixture of 0.1 g (0.2 mmol) of compound **III**, 1 ml of 70% acetic acid, and 94 mg of zinc chloride was stirred for 4 h at room temperature. The mixture was diluted with water (3 ml) and extracted with butyl alcohol (3 × 10 ml). The organic layer was washed with a saturated solution of NaCl (30 ml), dried over $MgSO_4$, and evaporated. The solid residue was subjected to chromatography in a column charged with 5 g of silica gel (eluent $CHCl_3$–MeOH, 7:1) to isolate 60 mg (60%) of initial compound **III** (R_f 0.6) and 35 mg (38%) of compound **IV** (R_f 0.3), mp 124–126°C, $[\alpha]_D^{15}$ = –15.5° (*c* = 1.5, MeOH) (cf. [6, 7]). IR spectrum (KBr), ν, cm^{-1}: 1650, 1710, 3400. UV spectrum: λ_{max} 244 nm (ε = 14150). ^1H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 1.00 s (3H, 19-H); 1.04 s (3H, 18-H); 1.20 s (3H, 21-H); 1.27 s and 1.30 s (6H, 26-H, 27-H); 0.82–2.70 m (18H, CH, CH_2), 3.63 m (1H, 22-H, $w_{1/2}$ = 5); 3.84 m (1H, 2-H, $w_{1/2}$ = 10); 3.94 m (1H, 3-H, $w_{1/2}$ = 4); 5.44 m (1H, 15-H, $w_{1/2}$ = 3). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 18.4 q (C^{18}), 20.8 q (C^{21}), 23.8 t (C^{11}), 27.3 t (C^{23}), 28.9 q (C^{19}), 29.8 q (C^{26}), 29.9 q (C^{27}), 31.8 t (C^{16}), 33.1 t (C^4), 39.7 t (C^7), 38.0 t (C^{12}), 38.3 t (C^1), 42.3 t (C^{24}), 44.2 s (C^{10}), 47.3 s (C^{13}), 54.0 d (C^5), 57.6 d (C^{17}), 68.6 d (C^3), 70.0 d (C^2), 71.3 s (C^{25}), 77.4 s (C^{20}), 78.6 d (C^{22}), 120.3 d (C^{15}), 123.7 s (C^8), 136.6 s (C^9), 149.5 s (C^{14}), 215.7 s (C^6).

(20*R*,22*R*)-2β,3β,25-Trihydroxy-20,22-*O*-isopropylidene-5β-cholesta-7,9,14-trien-6-one (V). A mixture of 0.1 g (0.2 mmol) of compound **III**, 0.05 g of 10% Pd/C, and 5 ml of chloroform was stirred at room temperature under hydrogen until the conversion of **III** reached ~50% (~3 days, TLC). The mixture was evaporated, and the residue (~2 ml) was subjected to chromatography in a column charged with 5 g of silica gel (eluent $CHCl_3$–MeOH, 7:1) to isolate 48 mg (48%) of initial compound **III** (R_f 0.6) and 49 mg (49%) of compound **V** (R_f 0.8), $[\alpha]_D^{18}$ = –113.0° (*c* = 0.8, CH_3OH). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.87 s (3H, 19-H); 1.02 s (3H, 18-H); 1.16 s (3H, 21-H); 1.20 s and 1.22 s (6H, 26-H, 27-H); 1.27 s and 1.40 s (6H, 20,22-Me_2CO_2); 0.71–2.86 m (14H, CH, CH_2), 3.39–4.12 m (3H, 22-H, 2-H, 3-H); 6.08 s (1H, 7-H); 6.25 m (1H, 15-H, $w_{1/2}$ = 4); 6.30 m (1H, 11-H, $w_{1/2}$ = 3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.6 q (C^{18}), 20.8 q (C^{21}), 24.4 t (C^{23}), 26.7 q (C^{19}), 28.8 q (C^{26}), 29.2 q (C^{27}), 30.0 t (C^{16}), 29.5 q and 29.7 q (20,22-**Me**$_2$$CO_2$), 31.8 t ($C^4$), 38.7 t ($C^{12}$), 41.0 t ($C^1$), 42.0 t ($C^{24}$), 43.8 s ($C^{10}$), 45.7 s ($C^{13}$), 49.4 d ($C^5$), 57.0 d ($C^{17}$), 66.9 d ($C^3$), 67.5 d ($C^2$), 70.3 s ($C^{25}$), 81.6 d ($C^{22}$), 82.9 s ($C^{20}$), 106.9 s (20,22-Me$_2$**C**$O_2$), 116.3 d ($C^7$), 128.9 d ($C^{15}$), 131.7 d ($C^{11}$), 135.2 s ($C^{14}$), 143.8 s ($C^8$), 145.4 s ($C^9$), 203.8 s ($C^6$). Found, %: C 72.23; H 8.97. $C_{30}H_{44}O_6$. Calculated, %: C 71.97; H 8.86.

Podecdysone B 20,22-acetonide 25-trifluoroacetate or (20*R*,22*R*)-2β,3β-dihydroxy-20,22-*O*-isopropylidene-25-trifluoroacetoxy-5β-cholesta-8,14-dien-6-one (IX). Compound **VIII** was synthesized by the procedure described in [10]; mp 104–106°C, $[\alpha]_D^{15}$ = –150.3° (*c* = 1.7, $CHCl_3$); ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 19.0 q (C^{18}), 20.5 t (C^{11}), 21.1 q (C^{21}), 23.1 t (C^{23}), 23.2 q (C^{19}), 25.0 q (C^{26}), 25.8 q (C^{27}), 26.7 t (C^{12}), 26.7 q and 28.8 q (20,22-**Me**$_2$$CO_2$), 31.6 t ($C^4$), 36.4 t ($C^{16}$), 38.1 t ($C^1$), 38.4 d ($C^9$), 38.5 s ($C^{10}$), 39.5 t ($C^{24}$), 47.5 s ($C^{13}$), 49.7 d ($C^5$), 57.7 d ($C^{17}$), 67.2 d ($C^3$), 67.7 d ($C^2$), 80.8 d ($C^{22}$), 83.0 s ($C^{20}$), 88.7 s ($C^{25}$), 107.1 s (20,22-Me$_2$**C**$O_2$), 114.3 q (**C**$F_3CO_2$, $^1J_{CF}$ = 286.0), 120.6 d (C^7), 128.4 d (C^{15}), 148.9 s (C^{14}), 155.6 s (C^8), 156.0 q (CF_3**C**O_2, $^2J_{CF}$ = 41.4), 203.6 s (C^6). A mixture of 0.2 g (0.33 mmol) of compound **VIII**, 0.05 g

* The signal from C^{13} is overlapped by the solvent multiplet (δ_C 49 ppm).

of 10% Pd/C, and 5 ml of chloroform was stirred at room temperature under hydrogen until the conversion of **VIII** reached 50% (~7 days, TLC). The mixture was evaporated, and the residue (~2 ml) was subjected to column chromatography on 8 g of silica gel using $CHCl_3$–MeOH (10 : 1) as eluent. We isolated 96 mg (48%) of initial compound **VIII** (R_f 0.5) and 93 mg (47%) of compound **IX** (R_f 0.6); mp 112–114°C; $[\alpha]_D^{18}$ = –35.4° (*c* = 1.1, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1710, 1730, 3400. UV spectrum, λ_{max}, nm: 302 (ε = 9356). ^1H NMR spectrum (C_5D_5N), δ, ppm (*J*, Hz): 1.19 s (3H, 19-H); 1.33 s (3H, 18-H); 1.41 s (3H, 21-H); 1.52 s and 1.54 s (6H, 20,22-Me_2CO_2); 1.59 s and 1.60 s (6H, 26-H, 27-H); 0.88–3.17 m (18H, CH, CH_2); 3.89 m (1H, 22-H, $w_{1/2}$ = 19); 4.38 m (1H, 2-H, $w_{1/2}$ = 9); 4.44 m (1H, 3-H, $w_{1/2}$ = 7); 5.36 m (1H, 15-H, $w_{1/2}$ = 30). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 17.8 q (C^{18}), 21.3 q (C^{21}), 23.5 t (C^{11}), 23.5 t (C^{23}), 24.9 q (C^{26}), 25.0 q (C^{19}), 25.3 q (C^{27}), 29.9 t (C^{16}), 26.9 q and 29.9 q (20,22-**Me**$_2CO_2$), 31.7 t (C^4), 36.7 t (C^{12}), 38.1 t (C^1), 39.1 t (C^7), 41.0 t (C^{24}), 43.4 s (C^{10}), 46.0 s (C^{13}), 53.3 d (C^5), 56.3 d (C^{17}), 68.0 d (C^3), 69.3 d (C^2), 81.2 d (C^{22}), 83.6 s (C^{20}), 89.7 s (C^{25}), 107.0 s (20,22-Me_2**C**O_2), 113.1 q (**C**F_3CO_2, $^1J_{CF}$ = 286.0), 118.7 d (C^{15}), 122.5 s (C^8), 136.6 s (C^9), 148.4 s (C^{14}), 155.9 q (CF_3**C**O_2, $^2J_{CF}$ = 41.4), 212.1 s (C^6). Found, %: C 64.50; H 7.69. $C_{32}H_{45}F_3O_7$. Calculated, %: C 64.20; H 7.58.

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