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First Example of Trifluoromethylation in the Ecdysteroid Series. Synthesis of (20*RS*)-20-*O*-Hydro-20-trifluoromethylpoststerone

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Abstract—The title compound was synthesized by trifluoromethylation of poststerone derivatives with trimethyl(trifluoromethyl)silane in the presence of tetrabutylammonium fluoride.

Replacement of a methyl group by trifluoromethyl, which has a comparable size but is strongly electron-acceptor and lipophilic, endows an organic molecule with new physical, chemical, and biological properties [1, 2]. Many procedures for introduction of trifluoromethyl group into organic compounds are known [3], but the most promising is the use of trimethyl(trifluoromethyl)silane as nucleophilic trifluoromethylating agent [2, 4]. This reagent is applicable to various organic compounds, including keto steroids [4]; however, no examples of trifluoromethylation in the series of ecdysteroids have so far been reported.

We previously found [5, 6] that polyhydroxysterols do not undergo trifluoromethylation if at least one hydroxy group is not protected [6]. In this case, trifluoromethylation of the hydroxy rather than keto group occurs [5, 6]. We have succeeded in effecting trifluoromethylation of 14α-*O*-trimethylsilylpoststerone diacetate **V** and acetonide **VI**. Compounds **V** and **VI** were synthesized by oxidative cleavage at the C^{20}–C^{22} bond [7] of 20-hydroxyecdysone (**I**) isolated from *Serratula coronata* [8]. The resulting poststerone **II** was converted into diacetate **III** and acetonide **IV** which were treated with Me_3SiCF_3 [5] to obtain ketones **V** and **VI**. Subsequent reactions of the latter with Me_3SiCF_3 in the presence of tetrabutylammonium fluoride gave the corresponding products of nucleophilic addition of CF_3 group at the C^{20}=O carbonyl group, (20*RS*)-14α,20-di-*O*-trimethylsilyl-20-(trifluoromethyl)poststerone diacetate **VII** and acetonide **VIII**. Here, the C^6=O group remains intact, as follows from the IR, UV, and ^1H and ^{13}C NMR spectra. The fact that the addition of Me_3SiCF_3 occurred just at the C^{20}=O group in **V** and **VI** is confirmed by the following data. The ^{13}C NMR spectra of the products lack signal at about δ_C 209 ppm, but two quartets appear at δ_C 78 ppm* (J = 26 Hz) and δ 126 ppm (J = 288 Hz), which belong to the CCF_3 fragment. In the ^1H NMR spectra of compounds **VII** and **VIII** we observed two singlets (1 : 1) in the δ range from 1.2 to 1.7 ppm with an overall intensity corresponding to three protons ($C^{21}H_3$) [instead of the singlet at δ 2.0 ppm from the acetyl group in the spectra of initial ketones **V** and **VI**), indicating that a new chiral (*RS*) center appeared at C^{20}.

Hydrolysis of diacetate **VII** with sodium hydroxide in aqueous methanol and of acetonide **VIII** with 70% acetic acid afforded diol **IX** which was treated with 5% hydrochloric acid in tetrahydrofuran in the presence of tetrabutylammonium fluoride to obtain the target trifluoromethyl-substituted poststerone analog, compound **X** (Scheme 1).

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer in mineral oil. The UV spectra were measured on a Specord M-40 spectrophotometer from solutions in methanol and chloroform. The ^1H and

* Insofar as the quartet signal from C^{20} at about δ_C 78 ppm in the ^{13}C NMR spectrum is partially overlapped by the solvent signal ($CDCl_3$), the spectrum of **VII** was also measured in benzene-d_6.

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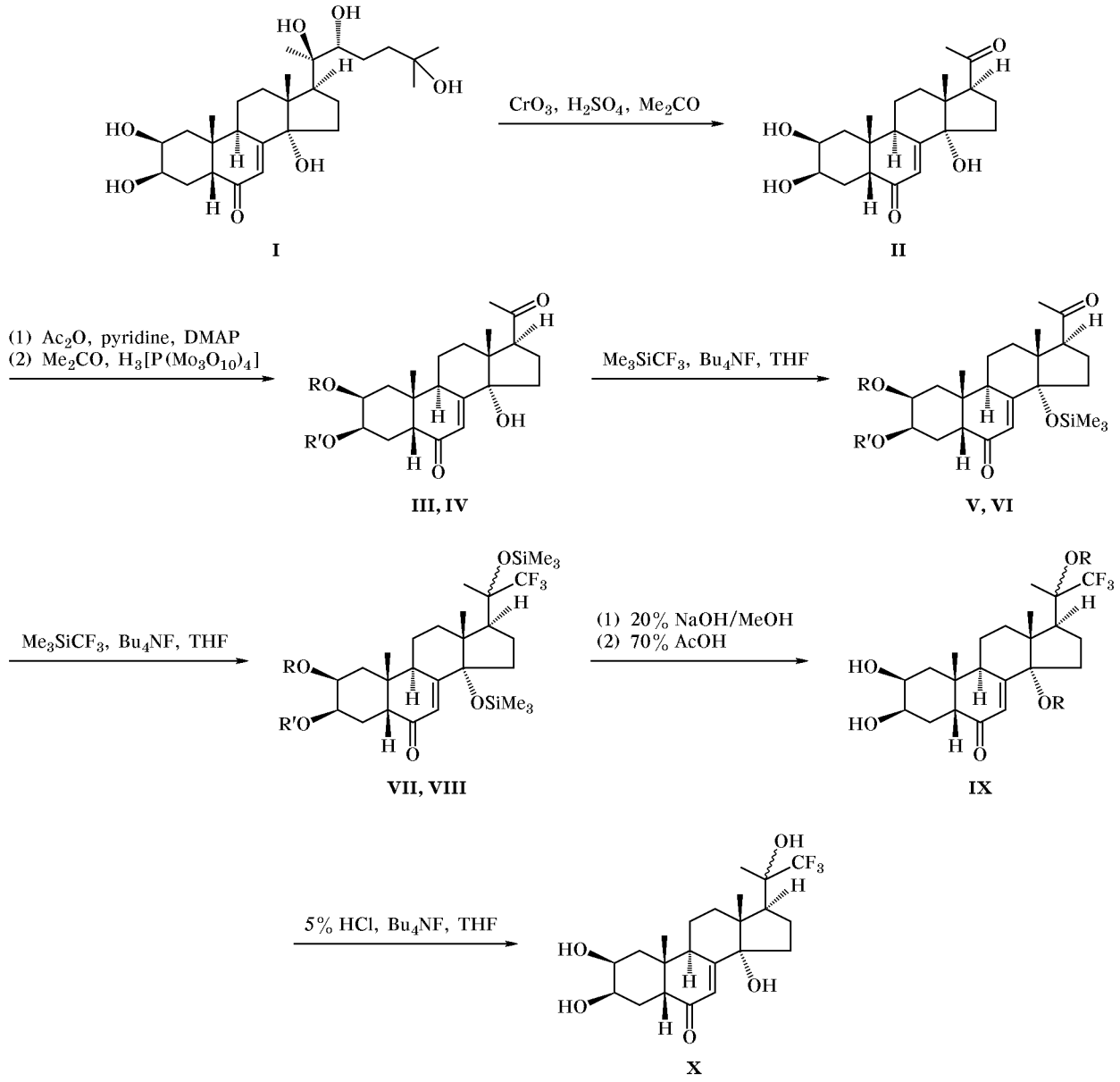
Scheme 1.



III, **V**, **VII**, R = R′ = Ac; **IV**, **VI**, **VIII**, RR′ = Me_2C; **IX**, R = $SiMe_3$.

^{13}C NMR spectra were obtained on a Bruker AM-300 instrument at 300.13 and 75 MHz, respectively, using chloroform-*d*, methanol-d_4, or benzene-d_6 as solvent; the chemical shifts were measured relative to tetramethylsilane as internal reference. The melting points were determined on a Boetius microdevice. The optical rotations were measured with the aid of a Perkin–Elmer 141 polarimeter. TLC analysis was performed on Silufol plates; spots were visualized by treatment with a solution of 4-hydroxy-3-methoxybenzaldehyde in ethanol, acidified with sulfuric acid.

2,3-Di-*O*-acetylpoststerone (or 2β,3β-diacetoxy-14α-hydroxy-5β-pregn-7-ene-6,20-dione) (III). Poststerone (**II**) was prepared according to the procedure described in [7] from 20-hydroxyecdysone (**I**) isolated from *Serratula coronata* [8]; mp 233–235°C (cf. [7]), $[\alpha]_D^{18}$ = +137.2° (*c* = 1.13, MeOH); the IR and ^1H and ^{13}C NMR spectra of **II** were identical to those reported in [9]. Compound **II**, 0.2 g (0.55 mmol), was dissolved in 2 ml of pyridine, 0.34 g (3.31 mmol) of acetic anhydride was added to the solution, and ~0.1 mg of 4-dimethylaminopyridine was then added

under stirring. After 3 h (TLC, eluent $CHCl_3$–MeOH, 5:1), the mixture was poured onto ice and extracted with $CHCl_3$ (3 × 10 ml), and the extract was washed with a saturated solution of sodium chloride (~5 ml), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (5 g; eluent $CHCl_3$). Yield of **III** 0.23 g (94%), R_f 0.58 ($CHCl_3$–MeOH, 5:1), mp 111–114°C, $[\alpha]_D^{24}$ = +106.1 (*c* = 1.48, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1250 ($OCOCH_3$); 1670, 1710 (C=CC=O); 1720 (C=O); 1750 ($COCH_3$). UV spectrum ($CHCl_3$), λ_{max}, nm (ε): 240 (12530). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.57 s (3H, $C^{18}H_3$), 0.98 s (3H, $C^{19}H_3$), 1.50–2.40 m (12H, CH_2), 1.97 s (3H, $C^{21}H_3$), 2.07 s and 2.11 s (6H, MeCO), 2.35 m (1H, 5-H), 3.12 m (1H, 9-H), 3.28 t (1H, 17-H, *J* = 8.0), 4.99 br.d (1H, 2-H, *J* = 12.1), 5.27 br.s (1H, 3-H), 5.82 br.s (1H, 7-H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 17.0 q (C^{18}), 20.4 t (C^{11}), 20.9 q and 21.0 q ($\mathbf{C}H_3CO$), 21.1 t (C^{16}), 23.7 q (C^{19}), 28.9 t (C^{15}), 29.6 t (C^{12}), 31.3 q (C^{21}), 31.7 t (C^4), 33.6 d (C^9), 33.8 t (C^1), 38.2 s (C^{10}), 47.5 s (C^{13}), 50.8 d (C^5), 58.6 d (C^{17}), 66.8 d (C^3), 68.6 d (C^2), 84.1 s (C^{14}), 121.7 d (C^7), 163.8 s (C^8), 170.2 s and 170.6 s ($\mathbf{C}H_3CO$), 202.1 s (C^6), 209.8 s (C^{20}). Found, %: C 67.32; H 7.62. $C_{25}H_{34}O_7$. Calculated, %: C 67.25; H 7.67.

2,3-*O*-Isopropylidenepoststerone (or 14α-hydroxy-2β,3β-isopropylidenedioxy-5β-pregn-7-ene-6,20-dione) (IV). Phosphomolybdic acid, 10.0 mg, was added to a suspension of 0.25 g (0.7 mmol) of poststerone (**II**) in 25 ml of anhydrous acetone. The mixture was stirred for 20 min at room temperature and evaporated under reduced pressure, 80 ml of water was added to the residue, and the mixture was neutralized with a saturated aqueous solution of $NaHCO_3$ and extracted with diethyl ether (3 × 10 ml). The combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (10 g; eluent $CHCl_3$–MeOH, 20:1). Yield of **IV** 0.2 g (73%), R_f 0.76 ($CHCl_3$–MeOH, 5:1), mp 183–184°C, $[\alpha]_D^{23}$ = +58° (*c* = 2.09, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1655 (C=CC=O), 1700 (C=O). UV spectrum ($CHCl_3$), λ_{max}, nm (ε): 240 (12390). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.60 s (3H, $C^{18}H_3$), 0.96 s (3H, $C^{19}H_3$), 1.32 s and 1.48 s (6H, Me_2C), 2.14 s (3H, $C^{21}H_3$), 1.20–2.40 m (13H, CH, CH_2), 2.85 m (1H, 9-H), 3.29 t (1H, 17-H, *J* = 8.0), 4.20 m (2H, 2-H, 3-H), 5.80 d (1H, 7-H, *J* = 2.5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.2 q (C^{18}), 20.6 t (C^{11}), 21.2 t (C^{16}), 23.6 q (C^{19}), 26.5 q ($\mathbf{Me}_2CO_2$), 26.7 t (C^{15}), 28.6 q ($\mathbf{Me}_2CO_2$), 30.0 t (C^{12}), 31.5 q (C^{21}), 32.0 t (C^4), 34.6 d (C^9), 37.6 t (C^1), 37.9 s (C^{10}), 47.9 s (C^{13}), 50.8 d (C^5), 58.8 d (C^{17}), 71.6 d (C^3), 72.1 d (C^2), 84.7 s (C^{14}), 108.4 s ($Me_2\mathbf{C}O_2$), 121.8 d (C^7), 162.3 s (C^8), 202.8 s (C^6), 209.6 s (C^{20}). Found, %: C 71.84; H 8.42. $C_{24}H_{34}O_5$. Calculated, %: C 71.61; H 8.51.

2,3-Di-*O*-acetyl-14-*O*-trimethylsilylpoststerone (or 2β,3β-acetoxy-14α-trimethylsiloxy-5α-pregn-7-ene-6,20-dione) (V). Tetrabutylammonium fluoride, 0.9 mg, was added with stirring at 0°C to a mixture of 0.2 g (0.45 mmol) of compound **III** and 0.19 g (1.35 mmol) of Me_3SiCF_3 in 3 ml of anhydrous THF. The reaction was complete in 3 min (TLC). The mixture was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (3 g) using $CHCl_3$ as eluent. Yield of **V** 0.22 g (95%), R_f 0.73 ($CHCl_3$–MeOH, 10:1), mp 77–80°C, $[\alpha]_D^{21}$ = +103° (*c* = 0.87, $CHCl_3$) (cf. [6]). The IR, UV, and ^1H and ^{13}C NMR spectra of the product were identical to those reported in [6].

2,3-*O*-Isopropylidene-14-*O*-trimethylsilylpoststerone (or 2β,3β-isopropylidenedioxy-14α-trimethylsiloxy-5β-pregn-7-ene-6,20-dione) (VI). Tetrabutylammonium fluoride, 0.4 mg, was added to a mixture of 0.074 g (0.18 mmol) of compound **IV** and 0.078 g (0.55 mmol) of Me_3SiCF_3 in 3 ml of anhydrous THF under stirring at 0°C. The reaction was complete in 3 min (TLC). The mixture was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (2 g) using $CHCl_3$ as eluent. Yield of **VI** 0.085 g (98%), R_f 0.79 ($CHCl_3$–MeOH, 20:1), mp 70–72°C, $[\alpha]_D^{23}$ = +40° (*c* = 1.75, $CHCl_3$) (cf. [6]). The IR, UV, and ^1H and ^{13}C NMR spectra of the product were identical to those reported in [6].

(20*RS*)-2,3-Di-*O*-acetyl-14α,20-di-*O*-trimethylsilyl-20-trifluoromethylpoststerone [or (20*RS*)-2β,3β-diacetoxy-14α,20-bis(trimethylsiloxy)-20-trifluoromethyl-5β-pregn-7-en-6-one] (VII). Tetrabutylammonium fluoride, 0.5 mg, was added to a mixture of 0.134 g (0.23 mmol) of compound **V** and 0.097 g (0.68 mmol) of Me_3SiCF_3 in 3 ml of anhydrous THF under stirring at 0°C. The reaction was complete in 3 min (TLC). The mixture was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (2 g) using $CHCl_3$ as eluent. Yield of **VII** 0.141 g (94%), R_f 0.72 ($CHCl_3$–MeOH, 20:1), mp 49–51°C, $[\alpha]_D^{23}$ = +27.1° (*c* = 2.4, $CHCl_3$). IR spectrum, ν,

cm^{-1}: 840 ($SiCH_3$); 1250 ($SiCH_3$, $OCOCH_3$); 1160, 1350 (CF_3); 1665 (C=CC=O). UV spectrum ($CHCl_3$), λ_{max}, nm (ε): 242 (15200). ^1H NMR spectrum, δ, ppm (*J*, Hz): in $CDCl_3$: 0.07 s and 0.12 s (18H, $SiMe_3$), 0.74 s (3H, $C^{18}H_3$), 1.23 s (3H, $C^{19}H_3$), 1.23 s and 1.41 s (3H, $C^{21}H_3$), 1.35–2.20 m (12H, CH_2), 1.99 s and 2.09 s (6H, MeCO), 2.35 m (2H, 5-H, 17-H), 2.98 m (1H, 9-H), 5.00 br.d (1H, 2-H, *J* = 1.2), 5.36 br.s (1H, 3-H), 5.84 br.s (1H, 7-H); in C_6D_6: 0.03 s and 0.60 s (18H, $SiMe_3$), 0.54 s (3H, $C^{18}H_3$), 0.87 s (3H, $C^{19}H_3$), 1.23 s (3H, $C^{21}H_3$), 1.72 s (6H, MeCO), 1.35–2.20 m (12H, CH_2), 2.37 br.d (1H, 17-H, *J* = 8.0), 2.56 m (1H, 5-H), 3.00 m (1H, 9-H), 5.17 m (1H, 2-H), 5.56 br.s (1H, 3-H), 5.86 br.s (1H, 7-H). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): in $CDCl_3$: 1.8 q and 2.0 q ($SiMe_3$), 16.3 q (C^{18}), 20.4 t (C^{11}), 21.1 q and 21.1 q (**C**H_3CO), 21.2 t (C^{16}), 22.4 q (C^{19}), 24.1 q (C^{21}), 29.2 t (C^{15}), 29.7 t (C^{12}), 31.3 t (C^4), 33.8 d (C^9), 33.9 t (C^1), 38.3 s (C^{10}), 48.9 d (C^{17}), 49.1 s (C^{13}), 50.9 d (C^5), 66.9 d (C^3), 68.6 d (C^2), 78.0 q (C^{20}, $^2J_{CF}$ = 26.0), 87.3 s (C^{14}), 122.8 d (C^7), 126.2 q (CF_3, $^1J_{CF}$ = 288), 163.7 s (C^8), 170.2 s and 170.3 s (CH_3**C**O), 201.8 s (C^6); in C_6D_6: 1.7 q and 2.0 q ($SiCH_3$), 16.3 q (C^{18}), 20.6 q and 20.7 q (**C**H_3CO), 21.6 t (C^{11}), 22.4 q (C^{19}), 23.1 t (C^{16}), 24.2 q (C^{21}), 29.8 t (C^{15}), 30.1 t (C^{12}), 31.5 t (C^4), 34.0 d (C^9), 34.5 t (C^1), 38.4 s (C^{10}), 49.2 s (C^{13}), 49.3 d (C^{17}), 51.4 d (C^5), 67.2 d (C^3), 69.0 d (C^2), 78.5 q (C^{20}, $^2J_{CF}$ = 26.0), 87.6 s (C^{14}), 123.0 d (C^7), 126.9 q (CF_3, $^1J_{CF}$ = 287), 161.8 s (C^8), 169.4 s and 169.7 s (CH_3**C**O), 199.9 s (C^6). Found, %: C 58.28; H 7.69. $C_{32}H_{51}F_3O_7Si_2$. Calculated, %: C 58.15; H 7.78.

(20*RS*)-2,3-*O*-Isopropylidene-14α,20-di-*O*-trimethylsilyl-20-trifluoromethylpoststerone [or (20*RS*)-2β,3β-isopropylidenedioxy-14α,20-bis(trimethylsiloxy)-20-trifluoromethyl-5β-pregn-7-en-6-one] (VIII). Tetrabutylammonium fluoride, 0.6 mg, was added to a mixture of 0.128 g (0.27 mmol) of compound **VI** and 0.115 g (0.81 mmol) of Me_3SiCF_3 in 3 ml of anhydrous THF under stirring at 0°C. The reaction was complete in 3 min (TLC). The mixture was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (3 g) using $CHCl_3$ as eluent. Yield of **VIII** 0.051 g (31%), R_f 0.63 ($CHCl_3$–MeOH, 40:1), mp 40–42°C, $[\alpha]_D^{21}$ = +31.4 (*c* = 2.54, $CHCl_3$). IR spectrum, ν, cm^{-1}: 850, 1245 (SiMe); 1145, 1350 (CF_3); 1650 (C=CC=O). UV spectrum ($CHCl_3$), λ_{max}, nm (ε): 244 (12500). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.08 s and 0.13 s (18H, $SiMe_3$), 0.71 s (3H, $C^{18}H_3$), 1.03 s (3H, $C^{19}H_3$), 1.34 s and 1.50 s (6H, Me_2C), 1.46 s and 1.73 s (3H, $C^{21}H_3$), 1.25–2.15 m (13H, CH, CH_2), 2.35 d.d (1H, 17-H, *J* = 8.0, 8.0), 2.67 m (1H, 9-H), 4.18 m (1H, 2-H), 4.28 m (1H, 3-H), 5.81 br.s (1H, 7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 1.7 q and 2.9 q ($SiMe_3$), 16.3 q (C^{18}), 21.0 t (C^{11}), 21.2 t (C^{16}), 23.3 q (C^{19}), 26.2 t (C^{15}), 26.3 q and 26.3 q (**Me**$_2$$CO_2$), 28.5 q ($C^{21}$), 29.7 t ($C^{12}$), 31.5 t ($C^4$), 35.9 d ($C^9$), 37.1 t ($C^1$), 37.4 s ($C^{10}$), 48.9 d ($C^{17}$), 49.9 s ($C^{13}$), 50.2 d ($C^5$), 71.5 d ($C^3$), 72.4 d ($C^2$), 78.1 q ($C^{20}$, $^2J_{CF}$ = 26), 87.6 s (C^{14}), 108.3 s (Me_2**C**O_2), 122.1 d (C^7), 126.2 q (CF_3, $^1J_{CF}$ = 288), 162.6 s (C^8), 202.1 s (C^6). Found, %: C 60.41; H 8.28. $C_{31}H_{51}F_3O_5Si_2$. Calculated, %: C 60.36; H 8.33.

(20*RS*)-14α,20-Bis-*O*-(trimethylsilyl)-20-trifluoromethylpoststerone [or (20*RS*)-β,3β-dihydroxy-14α,20-bis(trimethylsiloxy)-20-trifluoromethyl-5β-pregn-7-en-6-one (IX). *a*. To a solution of 0.098 g (0.15 mmol) of compound **VII** in 3 ml of methanol we added with stirring 0.1 ml of a 20% solution of sodium hydroxide. When the reaction was complete (TLC), the solvent (methanol) was distilled off, and the residue was diluted with water (5 ml) and extracted with ethyl acetate (3 × 10 ml). The combined extracts were washed with water (3 ml), dried over $MgSO_4$, and evaporated under reduced pressure. Yield of **IX** 0.74 g (87%), R_f 0.56 ($CHCl_3$–MeOH, 10:1), mp 108–110°C, $[\alpha]_D^{21}$ = +18.1° (*c* = 2.59, $CHCl_3$). IR spectrum, ν, cm^{-1}: 850, 1245 (SiMe); 1145, 1350 (CF_3); 1665 (C=CC=O). UV spectrum ($CHCl_3$), λ_{max}, nm (ε): 241 (13450). ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.06 s and 0.13 s (18H, $SiMe_3$), 0.69 s (3H, $C^{18}H_3$), 0.94 s (3H, $C^{19}H_3$), 1.25 s and 1.46 s (3H, $C^{21}H_3$), 1.30–2.40 m (13H, CH, CH_2), 2.48 m (1H, 5-H), 2.88 m (1H, 9-H), 3.80 m (1H, 2-H), 4.08 m (1H, 3-H), 5.84 br.s (1H, 7-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 1.7 q and 1.9 q ($SiMe_3$), 16.2 q (C^{18}), 21.1 t (C^{11}), 22.3 q (C^{19}), 22.6 t (C^{16}), 24.1 q (C^{21}), 29.3 t (C^{15}), 29.6 t (C^{12}), 31.2 t (C^4), 33.8 d (C^9), 36.7 t (C^1), 38.1 s (C^{10}), 48.9 d (C^{17}), 49.1 s (C^{13}), 49.8 d (C^5), 67.2 d (C^3), 68.0 d (C^2), 78.0 q (C^{20}, $^2J_{CF}$ = 26), 87.3 s (C^{14}), 122.4 d (C^7), 126.2 q (CF_3, $^1J_{CF}$ = 288), 164.0 s (C^8), 203.8 s (C^6). Found, %: C 58.53; H 8.16. $C_{28}H_{47}F_3O_5Si_2$. Calculated, %: C 58.30; H 8.21.

b. A mixture of 0.05 g (0.08 mmol) of compound **VIII** and 1 ml of 70% acetic acid was stirred for 1.5 h. The mixture was then diluted with 10 ml of water and extracted with 1-butanol (3 × 5 ml). The

combined extracts were washed with water (5 ml) and evaporated under reduced pressure. The residue was purified by column cromatography on silica gel (3 g) using $CHCl_3$–MeOH (20 : 1) as eluent. Yield 0.028 g (60%). The product was identical to a sample obtained as described above in *a*.

(20*RS*)-20-*O*-Hydro-20-trifluoromethylpoststerone [or (20*RS*)-2β,3β,14α,20-tetrahydroxy-20-trifluoromethyl-5β-pregn-7-en-6-one (X). A mixture of 0.046 g (0.08 mmol) of compound **IX**, 0.17 g of tetrabutylammonium fluoride, one drop of water, one drop of 5% hydrochloric acid, and 1 ml of THF was stirred for 4 h. Ethyl acetate, 5 ml, was added, and the mixture was washed with 3 ml of water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel (5 g) using $CHCl_3$–MeOH (10 : 1) as eluent. Yield of **X** 0.024 g (70%), R_f 0.22 ($CHCl_3$–MeOH, 5 : 1), mp 118–120°C, $[\alpha]_D^{20}$ = +31.8° (*c* = 1.1, $CHCl_3$). IR spectrum, ν, cm^{-1}: 1150, 1360 (CF_3); 1650 (C=CC=O). UV spectrum (MeOH), λ_{max}, nm (ε): 243 (11470). ^1H NMR spectrum (CD_3OD), δ, ppm (*J*, Hz): 0.87 s (3H, $C^{18}H_3$), 0.95 s (3H, $C^{19}H_3$), 1.45 s and 1.65 s (3H, $C^{21}H_3$), 1.18–2.17 m (13H, CH, CH_2), 2.37 d.d (1H, 17-H, *J* = 8.0, 8.0), 2.52 t (1H, 5-H, *J* = 8.9), 3.18 m (1H, 9-H), 3.82 m (1H, 2-H), 3.94 br.s (1H, 3-H), 5.81 d (1H, 7-H, *J* = 2.1). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 17.5 q (C^{18}), 20.8 t (C^{11}), 21.8 q (C^{19}), 24.5 q (C^{21}), 24.8 t (C^{16}), 31.9 t (C^{15}), 32.3 t (C^{12}), 32.9 t (C^4), 35.1 d (C^9), 37.4 t (C^1), 39.2 s (C^{10}), 51.8 d (C^5), 68.5 d (C^3), 68.7 d (C^2), 76.0 q (C^{20}, $^2J_{CF}$ = 25), 84.9 s (C^{14}), 122.4 d (C^7), 128.1 q (CF_3, $^1J_{CF}$ = 288), 167.5 s (C^8), 206.5 s (C^6); signals from C^{13} and C^{17} are overlapped by the solvent signal (δ_C 49 ppm). Found, %: C 61.25; H 7.14. $C_{22}H_{31}F_3O_5$. Calculated, %: C 61.10; H 7.22.

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