

# Ozonolysis of Alkenes and Study of Reactions of Polyfunctional Compounds: LXVII.\* Synthesis of 27,27,27-Trifluoro-20-hydroxyecdysone Acetonides from 24,25- and 25,26-Anhydro-20-hydroxyecdysone Derivatives via Ozonolysis and Trifluoromethylation

V. N. Odinokov, R. G. Savchenko, S. R. Afon'kina, and L. M. Khalilov

Institute of Petroleum Chemistry and Catalysis, Academy of Sciences of Bashkortostan Republic and Ufa Research Center, Russian Academy of Sciences, pr. Oktyabrya 141, Ufa, 450075 Bashkortostan, Russia  
e-mail: ink@anrb.ru

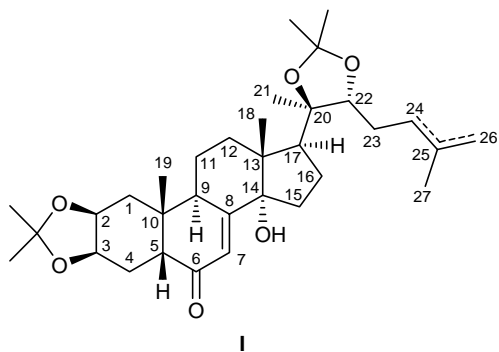
Received May 12, 2004

**Abstract**—Ozonolysis of 24,25/25,26-anhydro derivatives of 20-hydroxy-2,3:20,22-di-*O*-isopropylideneecdysone and 2,3-di-*O*-acetyl-20-hydroxy-20,22-*O*-isopropylideneecdysone, followed by trifluoromethylation of the corresponding 25-oxo derivatives afforded 2,3:20,22-di-*O*-isopropylidene- and 20,22-*O*-isopropylidene-27,27,27-trifluoro-20-hydroxyecdysones.

Introduction of a fluorine atom or a perfluoroalkyl group (in particular, trifluoromethyl) into molecules of organic compounds could essentially change their physical, chemical, and biological properties, thus giving rise to new ways of practical application, e.g., in medicine and agriculture [2, 3]. Several methods for the introduction of a trifluoromethyl group into organic molecules have been reported [4]. The most promising procedure for trifluoromethylation of carbonyl compounds is based on the use of (trifluoromethyl)trimethylsilane as CF<sub>3</sub> nucleophile [5, 6].

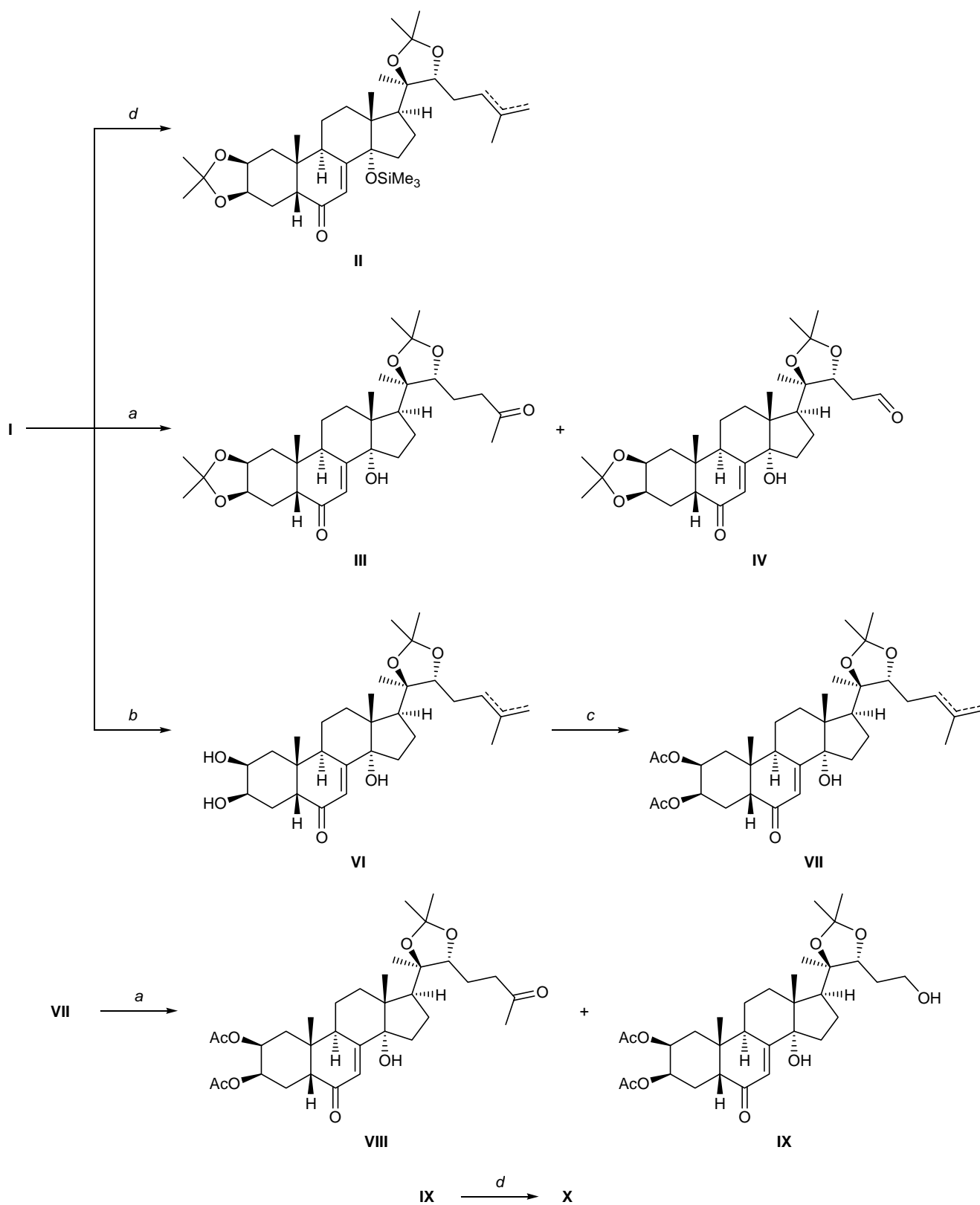
In the present work we examined trifluoromethylation of 25-oxo-27-norponasterone A derivatives obtained by ozonolysis of 24,25/25,26-anhydro-20-hydroxy-2,3:20,22-di-*O*-isopropylideneecdysone (**I**) [1] and

2,3-di-*O*-acetyl-24,25/25,26-anhydro-20-hydroxy-20,22-*O*-isopropylideneecdysone (**VII**). Compound **VII** was synthesized in two steps from diacetonide **I** (Scheme 1): in the first step, deprotection of the 2,3-dihydroxy fragment gave compound **VI** which was subjected to acetylation with acetic anhydride in pyridine in the presence of 4-dimethylaminopyridine. Ozonolysis of diacetonide **I** in methylene chloride in the presence of 2 equiv of acetic acid, followed by treatment with 4.5 equiv of sodium triacetoxohydroborate, afforded a mixture of ketone **III** and aldehyde **IV**; the latter was formed instead of the expected corresponding alcohol [7]. Mixture **III/IV** was separated by column chromatography. The yield of ketone **III** obtained by the procedure described in [7] was greater than in the synthesis by ozonolysis [8] which was used by us previously [1] for the same purpose. By treatment with Me<sub>3</sub>SiCF<sub>3</sub> in the presence of Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup> (according to [9]) compounds **I** and **III** were converted into the corresponding 14-*O*-trimethylsilyl derivatives **II** and **V**. As followed from the intensity ratio of the signals from C<sup>25</sup>=C<sup>24</sup>H (δ 5.18 ppm, t, <sup>3</sup>J = 7.0 Hz) and C<sup>25</sup>=C<sup>26</sup>H<sub>2</sub> (δ 4.71 and 4.75 ppm, two singlets) in the <sup>1</sup>H NMR spectrum of **II**, the ratio of the Δ<sup>24,25</sup>- and Δ<sup>25,26</sup>-moieties is equal to ~2:1. Ozonolysis of silyl derivative **II** under different conditions (by the procedures reported in [7, 8, 10]) led to formation of a complex mixture of products.



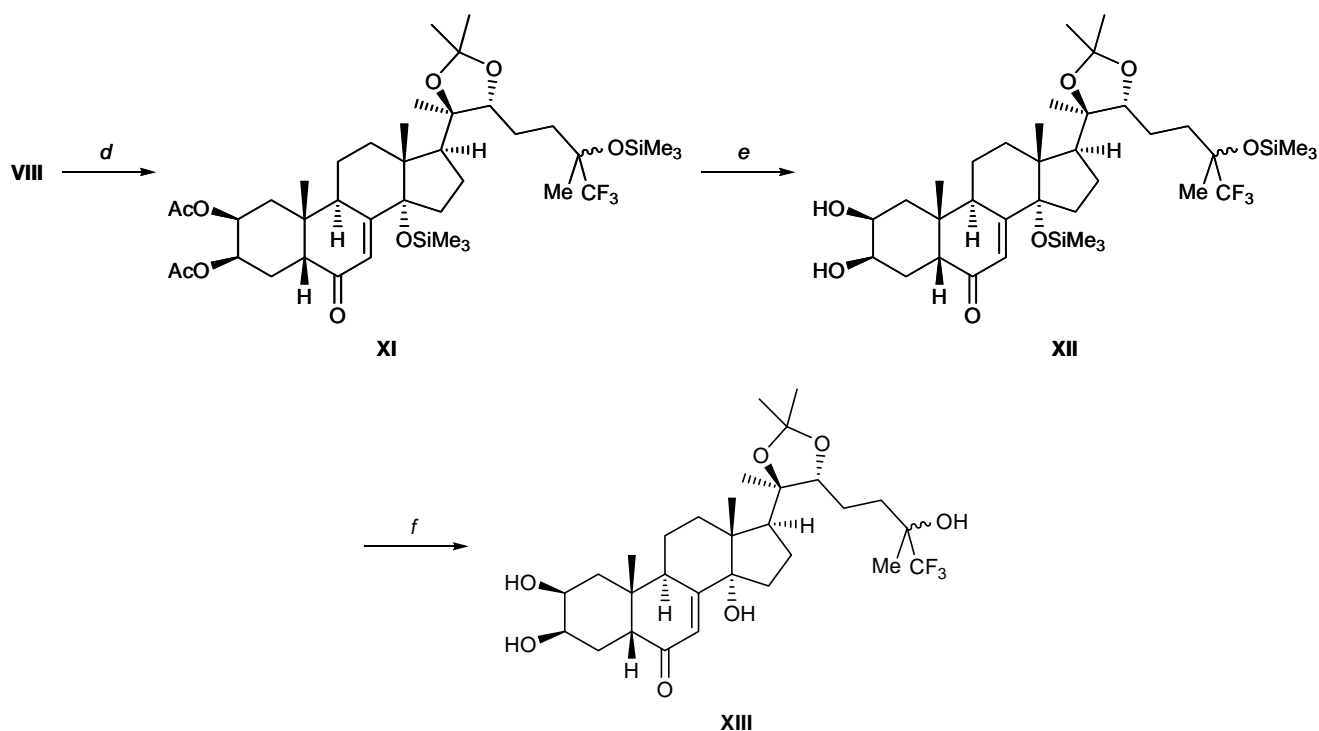
\* For communication LXVI, see [1].

Scheme 1.



*a:* (1) O<sub>3</sub>/AcOH, CH<sub>2</sub>Cl<sub>2</sub>; (2) NaBH(OAc)<sub>3</sub>; *b:* 70% AcOH; *c:* Ac<sub>2</sub>O, pyridine, 4-dimethylaminopyridine; *d:* Me<sub>3</sub>SiCF<sub>3</sub>, Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup>, THF.

Scheme 2.



*d:*  $\text{Me}_3\text{SiCF}_3$ ,  $\text{Bu}_4\text{N}^+\text{F}^-$ , THF; *e:* NaOH/MeOH; *f:* 5% HCl,  $\text{Bu}_4\text{N}^+\text{F}^-$ , THF.

Unlike compound I, ozonolysis of 2,3-diacetoxy derivative VII according to [7] gave the expected mixture of ketone VIII and alcohol IX, which were separated by column chromatography. Ketone VIII can readily be identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Its  $^{13}\text{C}$  NMR spectrum contained characteristic signals at  $\delta_{\text{C}}$  208.5 (O=C<sup>25</sup>), 202.3 (O=C<sup>6</sup>), 170.2 and 170.5 (OAc), 164.9 (C<sup>8</sup>), 121.4 (C<sup>7</sup>), and 107.0 ppm (O–C–O). Alcohol IX showed in the  $^{13}\text{C}$  NMR spectrum a signal at  $\delta$  61.4 ppm, which is typical of carbon atom at the primary hydroxy group (C<sup>24</sup>H<sub>2</sub>OH). Alcohol IX was converted into the corresponding 14,24-bis(trimethylsilyl) ether X according to the procedure described in [9]. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of X contained the following signals:  $\delta_{\text{C}}$  1.9 (14-OSiMe<sub>3</sub>), 0.6 ppm (24-OSiMe<sub>3</sub>) and  $\delta$  0.10 (9H, 14-OSiMe<sub>3</sub>), 0.09 ppm (9H, 24-OSiMe<sub>3</sub>) (cf. [9, 11]).

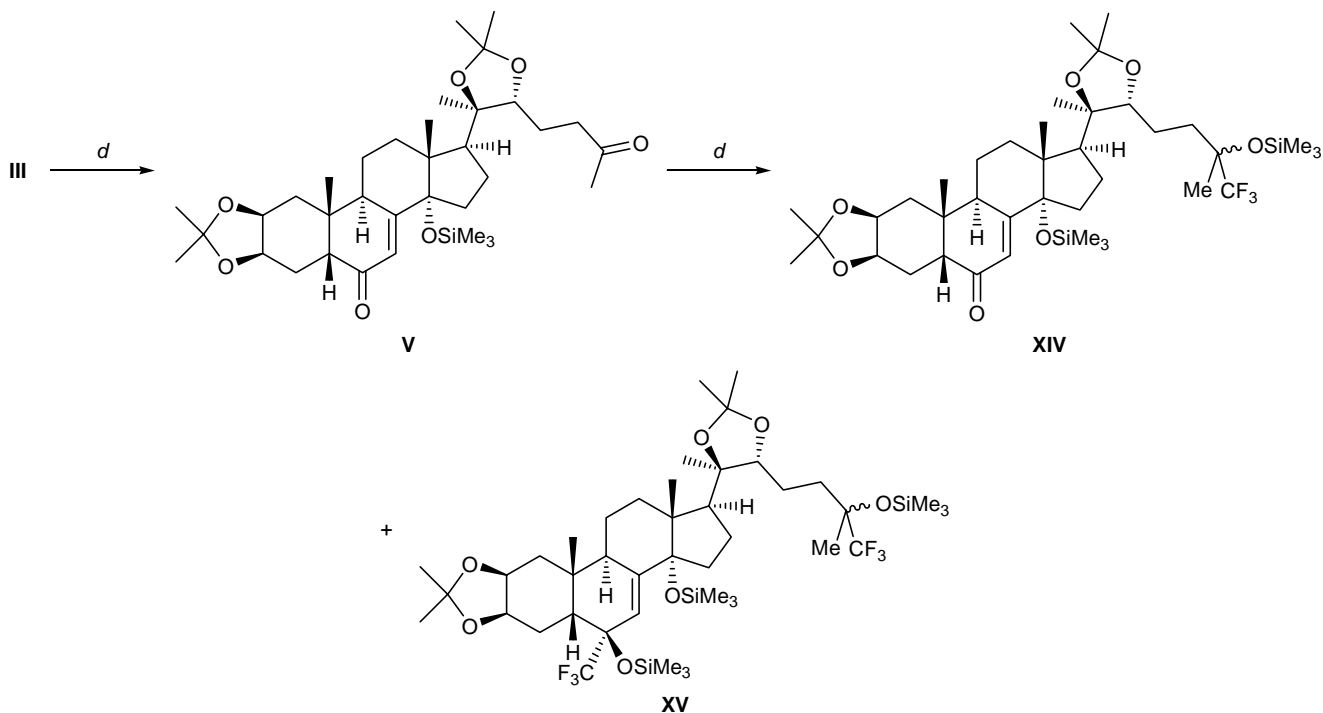
In the reaction of VIII with  $\text{Me}_3\text{SiCF}_3$  in the presence of  $\text{Bu}_4\text{N}^+\text{F}^-$ , only the side-chain keto group was involved, and the process was accompanied by silylation of the 14-hydroxy group. As a result, 2,3-di-*O*-acetyl-27,27,27-trifluoro-20-hydroxy-20,22-*O*-isopropylidene-14,25(*RS*)-di-*O*-trimethylsilyl-ecdysone (XI) was obtained (Scheme 2). The addition of  $\text{Me}_3\text{SiCF}_3$  to the C<sup>25</sup>=O keto group follows from the  $^1\text{H}$  and  $^{13}\text{C}$

NMR data. The  $^{13}\text{C}$  NMR spectrum of the trifluoromethylation product lacked carbonyl carbon signal at  $\delta_{\text{C}}$  208.5 ppm, while those corresponding to the CCF<sub>3</sub> moiety [quartets at  $\delta_{\text{C}}$  76.2 ( $^2J_{\text{CF}} = 28$  Hz) and 126.7 ppm ( $^1J_{\text{CF}} = 298$  Hz)] and two signals (1:1) from the OSiMe<sub>3</sub> group on (*RS*)-C<sup>25</sup> ( $\delta_{\text{C}}$  2.0 and 2.1 ppm) were present. Silylation of the 14-hydroxy group leads to a downfield shift of the C<sup>14</sup> signal ( $\Delta\delta_{\text{C}} = 3.3$  ppm) and appearance of a signal at  $\delta_{\text{C}}$  1.6 ppm due to the 14-OSiMe<sub>3</sub> group (cf. [11]).

Diacetate XI was converted into diol XII by treatment with sodium hydroxide in methanol (Scheme 2), and hydrolysis of the trimethylsilyloxy groups in XII by the action of dilute hydrochloric acid in the presence of  $\text{Bu}_4\text{N}^+\text{F}^-$  gave compound XIII. Acetonide XIII remained unchanged upon treatment with 70% acetic acid in the presence of  $\text{ZnCl}_2$  [12], i.e., under the conditions typical of hydrolysis of 20,22-*O*-isopropylidene derivatives of ecdysteroids. The overall yield of compound XIII in the six-step synthesis was 22.5%, calculated on initial compound I.

The reaction of V with  $\text{Me}_3\text{SiCF}_3$ - $\text{Bu}_4\text{N}^+\text{F}^-$  gave a mixture of mono- and bis-trifluoromethylation products, compounds XIV (at the C<sup>25</sup>=O group) and XV (at C<sup>25</sup>=O and C<sup>6</sup>=O) (Scheme 3). We succeeded in

Scheme 3.

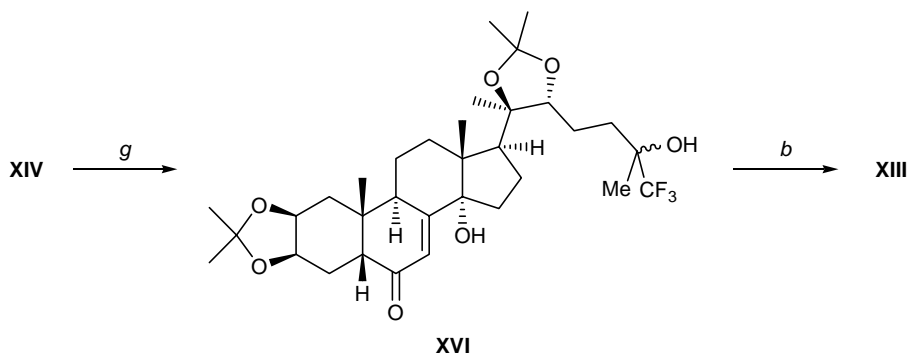


*d*:  $\text{Me}_3\text{SiCF}_3$ ,  $\text{Bu}_4\text{N}^+\text{F}^-$ , THF.

isolating by column chromatography pure compound **XV** and a mixture of **XIV** and **XV** at a ratio of ~2:1 (according to the 7-H signal intensities in the  $^1\text{H}$  NMR spectrum,  $\delta$  5.8 and 5.4 ppm). Mixture **XIV/XV** was treated with  $\text{Bu}_4\text{N}^+\text{F}^-$  in aqueous THF, and the subsequent chromatographic separation in a column charged with silica gel afforded 27,27,27-trifluoro-20-hydroxy-2,3:20,22-di-*O*-isopropylideneecdysone (**XVI**). Acid hydrolysis of the latter gave the corresponding mono-isopropylidene derivative **XIII** (Scheme 4) which was identical to that synthesized from compound **VIII**. The overall yield of **XIII** in the five-step synthesis was 5.6%, calculated on initial ecdysone derivative **I**.

The structure of compound **XV** is confirmed by the spectral data. In the  $^{13}\text{C}$  NMR spectrum of **XV** we observed no carbonyl carbon signals ( $\text{C}^{25}$  and  $\text{C}^6$ ,  $\delta_{\text{C}}$  207.9 and 202.0 ppm, respectively, in the spectrum of **V**), while signals from the doubly bonded  $\text{C}^7$  and  $\text{C}^8$  were displaced strongly upfield [ $\Delta\delta(\text{C}^8) = 15.0$ ,  $\Delta\delta(\text{C}^7) = 7.9$  ppm]; the  $\text{C}^6\text{-CF}_3$  and  $\text{C}^{25}\text{-CF}_3$  groups gave rise to a quartet at  $\delta_{\text{C}}$  126.3 ppm ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 286$  Hz) and two quartets at  $\delta_{\text{C}}$  75.8 ( $^2J_{\text{CF}} = 26$  Hz) and 75.9 ppm ( $^2J_{\text{CF}} = 28$  Hz). The presence of a double set of signals from the  $\text{C}^{26}\text{H}_3$  group in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra ( $\delta_{\text{C}}$  24.9 and 26.8 ppm,  $\delta$  1.22 and 1.26 ppm) suggests formation of a diastereoisomeric

Scheme 4.



*b*: 70% AcOH; *g*:  $\text{Bu}_4\text{N}^+\text{F}^-$ , THF- $\text{H}_2\text{O}$ .

mixture with respect to C<sup>25</sup>. On the other hand, closely located C<sup>5</sup> ( $\delta_C$  44.2 ppm), C<sup>7</sup> (113.9 ppm), C<sup>8</sup> (147.8 ppm), C<sup>9</sup> (39.2 ppm), and C<sup>10</sup> (32.3 ppm) atoms each give only one signal, indicating the same configuration of the C<sup>6</sup> chiral center. The 9-H and C<sup>9</sup> signals are displaced downfield ( $\Delta\delta = 1.10$  ppm,  $\Delta\delta_C = 2.88$  ppm) relative to the corresponding signals in the spectra of precursor **V** [11] due to deshielding effect of the  $\alpha$ -oriented pseudoaxial electron-acceptor trifluoromethyl group. Likewise, the OSiMe<sub>3</sub> group shields the C<sup>5</sup> and C<sup>10</sup> nuclei, so that their signals appear in a stronger field ( $\Delta\delta = 5.98$  and 5.02 ppm, respectively), in keeping with the  $\beta$ -orientation and pseudo-equatorial position of the trimethylsiloxy group in the cyclohexene ring. Protons of the C<sup>19</sup>H<sub>3</sub> group also suffer from shielding effect by the Me<sub>3</sub>SiO group, and the corresponding singlet in the <sup>1</sup>H NMR spectrum of **XV** shifts upfield ( $\Delta\delta = 0.78$  ppm).

A strong support to the assumed structure of **XV** was obtained by chemical ionization mass spectrometry (MS-CI). The spectrum of **XV** recorded with the use of ammonia as reactant gas contained an ion peak with  $m/z$  918 [ $M + NH_4$ ]<sup>+</sup>, while the most abundant was that with  $m/z$  828 [ $M + H - Me_3Si$ ]<sup>+</sup>. In the CI mass spectrum recorded with methane as reactant gas, an ion peak with  $m/z$  916 [ $M + CH_4$ ]<sup>+</sup> was present, and the ion with  $m/z$  827 [ $M - Me_3Si$ ]<sup>+</sup> was the most abundant.

## EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples pelleted with KBr. The UV spectra were measured on a Specord M-40 spectrophotometer from solutions in chloroform. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker AM-300 instrument at 300.13 and 75 MHz, respectively, using CDCl<sub>3</sub> as solvent; the chemical shifts were measured relative to tetramethylsilane as internal reference. The chemical ionization mass spectra were run on a Riber 10-10B spectrometer (Nermag S.A.) using NH<sub>3</sub> and CH<sub>4</sub> as reactant gases. The melting points were determined on a Boetius micro device. The optical rotations were measured on a Perkin-Elmer-141 polarimeter. Thin-layer chromatography was performed on Silufol plates; spots were visualized by spraying with a solution of vanillin in ethanol acidified with sulfuric acid.

**(20R,22R)-2 $\beta$ ,3 $\beta$ :20,22-bis(isopropylidenedioxy)-14 $\alpha$ -trimethylsiloxy-5 $\beta$ -cholesta-7,24(or 25)-dien-6-one (II).** A mixture of 1.0 g (1.85 mmol) of compound **I** ( $\Delta^{24}/\Delta^{25}$  isomer mixture prepared as described in [1])

and 0.79 g (5.54 mmol) of Me<sub>3</sub>SiCF<sub>3</sub> in 5 ml of anhydrous THF was cooled to 0°C, and 3.9 mg (0.8 mol %) of Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup> was added under stirring. 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 (5 g) using chloroform as eluent to isolate 1.03 g (91%) of compound **II** ( $\Delta^{24}/\Delta^{25}$  isomer mixture at a ratio of 2:1).  $R_f$  0.74 (CHCl<sub>3</sub>-MeOH, 10:1), mp 76–79°C,  $[\alpha]_D^{25} = 60.4^\circ$  ( $c = 2.11$ , CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 840 and 1250 (SiCH<sub>3</sub>), 1670 (C=C-C=O). UV spectrum:  $\lambda_{max}$  240 nm ( $\epsilon = 12530$ ). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.07 s and 0.08 s (9H, Me<sub>3</sub>Si); 0.72 s (3H, C<sup>18</sup>H<sub>3</sub>); 1.03 s and 1.04 s (3H, C<sup>19</sup>H<sub>3</sub>); 1.12 s and 1.14 s (3H, C<sup>21</sup>H<sub>3</sub>); 1.31 s, 1.32 s, 1.40 s, and 1.49 s (12H, Me<sub>2</sub>C); 1.64 s and 1.73 s (~5H, C<sup>27</sup>H<sub>3</sub>); 1.58–2.12 m (~14.5H, CH<sub>2</sub>); 2.15–2.20 m (1H, 17-H); 2.36 d.d (1H, 5-H, <sup>3</sup> $J = 10.5$ , 5.0 Hz); 2.63 d.d (1H, 9-H, <sup>3</sup> $J = 11.4$ , 8.7 Hz); 3.64–3.70 m (1H, 22-H); 4.14–4.19 m (1H, 2-H); 4.21–4.26 m (1H, 3-H); 4.71 br.s and 4.75 br.s (~0.7H, C<sup>26</sup>H<sub>2</sub>,  $\omega_{1/2} = 6.0$  Hz); 5.18 t (~0.7H, 24-H, <sup>3</sup> $J = 7.0$  Hz); 5.80 br.s (1H, 7-H,  $\omega_{1/2} = 8.4$  Hz). <sup>13</sup>C NMR spectrum,  $\delta_C$ , ppm: 1.8 q (Me<sub>3</sub>Si); 16.3 q (C<sup>18</sup>); 16.4 q (C<sup>27</sup>-C<sup>25</sup>=C<sup>26</sup>); 17.9 q (C<sup>27</sup>-C<sup>25</sup>=C<sup>24</sup>); 21.1 t and 21.2 t (C<sup>16</sup>); 21.4 t (C<sup>11</sup>); 22.5 q (C<sup>21</sup>); 24.0 q (C<sup>19</sup>); 25.9 q (C<sup>26</sup>-C<sup>25</sup>=C<sup>24</sup>); 26.1 t and 26.7 t (C<sup>23</sup>); 26.3 q, 26.8 q, 28.5 q, and 28.9 q (Me<sub>2</sub>C); 28.0 t (C<sup>15</sup>); 29.0 d (C<sup>9</sup>); 29.4 t and 29.5 t (C<sup>12</sup>); 31.2 t (C<sup>4</sup>); 34.8 t (C<sup>24</sup>-C<sup>25</sup>=C<sup>26</sup>); 36.9 t and 37.0 t (C<sup>1</sup>); 37.2 s and 37.3 s (C<sup>10</sup>); 49.1 d and 49.2 d (C<sup>17</sup>); 49.6 s and 49.8 s (C<sup>13</sup>); 50.0 d and 50.1 d (C<sup>5</sup>); 71.4 d (C<sup>3</sup>); 72.4 d (C<sup>2</sup>); 80.3 d and 80.9 d (C<sup>22</sup>); 83.9 s and 84.1 s (C<sup>20</sup>); 88.0 s (C<sup>14</sup>); 106.7 s (20,22-*O*-Me<sub>2</sub>C); 108.2 s (2,3-*O*-Me<sub>2</sub>C); 110.3 t (C<sup>26</sup>=C<sup>25</sup>); 120.0 d (C<sup>7</sup>); 121.7 d (C<sup>24</sup>=C<sup>25</sup>); 133.4 s (C<sup>25</sup>=C<sup>24</sup>); 145.0 s (C<sup>25</sup>=C<sup>26</sup>); 163.1 s and 163.2 s (C<sup>8</sup>); 202.1 s and 202.2 s (C<sup>6</sup>). Found, %: C 70.39; H 9.42. C<sub>36</sub>H<sub>58</sub>O<sub>6</sub>Si. Calculated, %: C 70.32; H 9.51.

**(20R,22R)-14 $\alpha$ -Hydroxy-2 $\beta$ ,3 $\beta$ :20,22-bis(isopropylidenedioxy)-27-nor-5 $\beta$ -cholest-7-ene-6,25-dione (III) and (20R,22R)-14 $\alpha$ -hydroxy-2 $\beta$ ,3 $\beta$ :20,22-bis(isopropylidenedioxy)-24-oxo-25,26,27-trinor-5 $\beta$ -cholest-7-en-6-one (IV).** An ozone-oxygen mixture was passed at a flow rate of 10 ml/min over a period of 40 s through a solution of 0.14 g (0.26 mmol) of compound **I** ( $\Delta^{24}/\Delta^{25}$  isomer mixture) and 0.031 g (0.52 mmol) of glacial acetic acid in 2 ml of methylene chloride under vigorous stirring and cooling to -2°C (until 0.30 mmol of O<sub>3</sub> was absorbed). The mixture was purged with argon and was slowly added under stirring to a suspension of NaBH(OAc)<sub>3</sub> in methylene

chloride [prepared by adding a solution of 0.21 g (3.50 mmol) of glacial acetic acid in 1 ml of methylene chloride to a suspension of 0.045 g (1.17 mmol) of  $\text{NaBH}_4$  in 2 ml of methylene chloride, followed by stirring for 2 h], cooled to 10°C. The mixture was stirred for 3 h at 20°C, and a solution of 0.08 g of sodium hydroxide in 2 ml of water was added. The organic phase was washed with water (3×2 ml) and evaporated on a rotary evaporator, and the residue was subjected to column chromatography on silica gel (5 g) using chloroform as eluent to isolate 0.05 g (36%) of ketone **III** [ $R_f$  0.66 ( $\text{CHCl}_3$ -MeOH, 10:1), mp 113–115°C,  $[\alpha]_D^{22} = 46.4^\circ$  ( $c = 1.7$ ,  $\text{CHCl}_3$ )] and 0.06 g (45%) of aldehyde **IV** [ $R_f$  0.48 ( $\text{CHCl}_3$ -MeOH, 10:1), mp 129–131°C,  $[\alpha]_D^{22} = 56.9^\circ$  ( $c = 2.5$ ,  $\text{CHCl}_3$ )]. The IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds **III** and **IV** were identical to those given in [1].

**(20R,22R)-2 $\beta$ ,3 $\beta$ :20,22-bis(isopropylidenedioxy)-14 $\alpha$ -trimethylsiloxy-27-nor-5 $\beta$ -cholest-7-ene-6,25-dione (V).** Tetrabutylammonium fluoride, 0.4 mg (0.8 mol %), was added under stirring at 0°C to a mixture of 0.1 g (0.18 mmol) of ketone **III** and 0.078 g (0.55 mmol) of  $\text{Me}_3\text{SiCF}_3$  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 chloroform as eluent to isolate 0.107 g (95%) of ketone **V**.  $R_f$  0.62 ( $\text{CHCl}_3$ -MeOH, 20:1), mp 81–84°C,  $[\alpha]_D^{25} = 53.3^\circ$  ( $c = 3.52$ ,  $\text{CHCl}_3$ ). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 840, 1250 ( $\text{SiCH}_3$ ); 1664 ( $\text{C}=\text{C}-\text{C}=\text{O}$ ); 1700 ( $\text{C}=\text{O}$ ). UV spectrum:  $\lambda_{\text{max}}$  242 nm ( $\epsilon = 12900$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.10 s (9H,  $\text{Me}_3\text{Si}$ ); 0.72 s (3H,  $\text{C}^{18}\text{H}_3$ ); 1.03 s (3H,  $\text{C}^{19}\text{H}_3$ ); 1.12 s (3H,  $\text{C}^{21}\text{H}_3$ ); 1.28 s, 1.33 s, 1.38 s, and 1.49 s (12H,  $\text{Me}_2\text{C}$ ); 1.25–2.18 m (16H, CH,  $\text{CH}_2$ ); 2.16 s (3H,  $\text{C}^{26}\text{H}_3$ ); 2.36 d.d (1H, 5-H,  $^3J = 10.7$ , 4.9 Hz); 2.49–2.65 m (2H, 9-H, 17-H); 3.62 d.d (1H, 22-H,  $^3J = 2.3$ , 10.0 Hz); 4.17 m (1H, 2-H); 4.23 m (1H, 3-H); 5.79 d (1H, 7-H,  $^4J = 1.7$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_C$ , ppm: 1.8 q ( $\text{Me}_3\text{Si}$ ); 16.3 q ( $\text{C}^{18}$ ); 21.2 t ( $\text{C}^{11}$ ); 21.4 t ( $\text{C}^{16}$ ); 21.9 q ( $\text{C}^{21}$ ); 22.7 t ( $\text{C}^{23}$ ); 24.0 q ( $\text{C}^{19}$ ); 26.2 t ( $\text{C}^{15}$ ); 26.3 q, 26.8 q, 28.5 q, and 28.9 q ( $\text{Me}_2\text{C}$ ); 29.5 t ( $\text{C}^{12}$ ); 30.0 q ( $\text{C}^{26}$ ); 31.3 t ( $\text{C}^4$ ); 36.4 d ( $\text{C}^9$ ); 37.1 t ( $\text{C}^1$ ); 37.3 s ( $\text{C}^{10}$ ); 40.9 t ( $\text{C}^{24}$ ); 49.1 d ( $\text{C}^{17}$ ); 49.7 s ( $\text{C}^{13}$ ); 50.1 d ( $\text{C}^5$ ); 71.5 d ( $\text{C}^3$ ); 72.5 d ( $\text{C}^2$ ); 80.3 d ( $\text{C}^{22}$ ); 84.2 s ( $\text{C}^{20}$ ); 88.1 s ( $\text{C}^{14}$ ); 106.9 s (20,22-*O*- $\text{CMe}_2$ ); 108.2 s (2,3-*O*- $\text{CMe}_2$ ); 121.8 d ( $\text{C}^7$ ); 163.0 s ( $\text{C}^8$ ); 202.0 s ( $\text{C}^6$ ); 207.9 s ( $\text{C}^{25}$ ). Found, %: C 68.28; H 9.05.  $\text{C}_{35}\text{N}_5\text{O}_7\text{Si}$ . Calculated, %: C 68.14; H 9.15.

**(20R,22R)-2 $\beta$ ,3 $\beta$ ,14 $\alpha$ -Trihydroxy-20,22-isopropylidenedioxy-5 $\beta$ -cholesta-7,24(or 25)dien-6-one**

**(VI).** A mixture of 0.35 g (0.65 mmol) of compound **I** ( $\Delta^{24}/\Delta^{25}$  isomer mixture) and 3 ml of 70% acetic acid was stirred at room temperature until the substrate conversion was complete (1.5 h, TLC). The mixture was diluted with water (3 ml) and extracted with diethyl ether (3×10 ml), and the extracts were combined, washed with a saturated solution of sodium chloride, and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel (4 g) using  $\text{CHCl}_3$ -MeOH (10:1) as eluent to isolate 0.322 g (99%) of compound **VI** ( $\Delta^{24}/\Delta^{25}$  isomer mixture at a ratio of ~2:1),  $R_f$  0.11, mp 135–137°C,  $[\alpha]_D^{23} = 56.2^\circ$  ( $c = 3.07$ ,  $\text{CHCl}_3$ ). IR spectrum:  $\nu(\text{C}=\text{C}-\text{C}=\text{O})$  1670  $\text{cm}^{-1}$ . UV spectrum:  $\lambda_{\text{max}}$  240 nm ( $\epsilon = 10891$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.77 s (3H,  $\text{C}^{18}\text{H}_3$ ), 0.94 s (3H,  $\text{C}^{19}\text{H}_3$ ), 1.15 s (3H,  $\text{C}^{21}\text{H}_3$ ), 1.32 s (~2H,  $\text{C}^{24}=\text{C}^{25}-\text{C}^{27}\text{H}_3$ ), 1.39 s and 1.62 s (6H,  $\text{Me}_2\text{C}$ ), 1.69 s (~2H,  $\text{C}^{26}\text{H}_3$ ), 1.70–2.15 m (~14.7H,  $\text{CH}_2$ ), 1.72 s (~1H,  $\text{C}^{26}=\text{C}^{25}-\text{C}^{27}\text{H}_3$ ), 2.20–2.27 m (1H, 17-H), 2.35–2.39 m (1H, 5-H), 3.05 m (1H, 9-H,  $\omega_{1/2} = 23$  Hz), 3.67 m (1H, 22-H,  $\omega_{1/2} = 25$  Hz), 3.87 m (1H, 2-H,  $\omega_{1/2} = 22$  Hz), 3.96 m (1H, 3-H,  $\omega_{1/2} = 10$  Hz), 4.69 br.s and 4.72 br.s (~0.7H,  $=\text{C}^{26}\text{H}_2$ ,  $\omega_{1/2} = 7.0$ , 7.0 Hz), 5.17 m (~0.7H,  $\text{C}^{25}=\text{C}^{24}\text{H}$ ), 5.80 br.s (1H, 7-H,  $\omega_{1/2} = 7$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_C$ , ppm: 17.0 q ( $\text{C}^{18}$  and  $\text{C}^{27}-\text{C}^{25}=\text{C}^{26}$ ), 18.0 q ( $\text{C}^{27}-\text{C}^{25}=\text{C}^{24}$ ), 20.8 t ( $\text{C}^{16}$ ), 21.1 t ( $\text{C}^{11}$ ), 22.6 q ( $\text{C}^{21}$ ), 23.8 q ( $\text{C}^{19}$ ), 25.7 q ( $\text{C}^{26}-\text{C}^{25}=\text{C}^{24}$ ), 26.1 t ( $\text{C}^{23}$ ), 26.6 q and 28.9 q ( $\text{Me}_2\text{C}$ ), 27.6 t ( $\text{C}^{15}$ ), 30.0 t ( $\text{C}^{12}$ ), 30.1 t ( $\text{C}^4$ ), 33.6 d ( $\text{C}^9$ ), 35.0 t ( $\text{C}^{24}-\text{C}^{25}=\text{C}^{26}$ ), 36.2 t ( $\text{C}^1$ ), 38.1 s ( $\text{C}^{10}$ ), 47.1 s ( $\text{C}^{13}$ ), 49.0 d ( $\text{C}^{17}$ ), 49.9 d ( $\text{C}^5$ ), 67.3 d ( $\text{C}^3$ ), 67.6 d ( $\text{C}^2$ ), 80.7 d and 81.0 d ( $\text{C}^{22}$ ), 84.1 s ( $\text{C}^{20}$ ), 84.5 s ( $\text{C}^{14}$ ), 106.8 s ( $\text{Me}_2\text{C}$ ), 109.9 t ( $\text{C}^{26}=\text{C}^{25}$ ), 120.4 d ( $\text{C}^7$ ), 121.2 d ( $\text{C}^{24}=\text{C}^{25}$ ), 133.5 s ( $\text{C}^{25}=\text{C}^{24}$ ), 145.3 s ( $\text{C}^{25}=\text{C}^{26}$ ), 166.3 s ( $\text{C}^8$ ), 204.9 s ( $\text{C}^6$ ). Found, %: C 71.72; H 9.17.  $\text{C}_{30}\text{H}_{46}\text{O}_6$ . Calculated, %: C 71.68; H 9.22.

**(20R,22R)-2 $\beta$ ,3 $\beta$ -Diacetoxy-14 $\alpha$ -hydroxy-20,22-isopropylidenedioxy-5 $\beta$ -cholesta-7,24(or 25)dien-6-one (VII).** Acetic anhydride, 0.309 g (3.03 mmol), and 4-dimethylaminopyridine, ~0.1 mg, were added in succession under stirring to a mixture of 0.254 g (0.51 mmol) of compound **VI** and 3 ml of pyridine. The reaction was complete in 3 h (TLC,  $\text{CHCl}_3$ -MeOH, 10:1). The mixture was diluted with 5 ml of water and extracted with diethyl ether (3×10 ml), and the extract was washed with a saturated solution of sodium chloride (~5 ml), dried over  $\text{MgSO}_4$ , and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel (5 g) using chloroform as eluent to isolate 0.284 g (96%) of

compound **VII** ( $\Delta^{24}/\Delta^{25}$  isomer mixture at a ratio of ~2:1),  $R_f$  0.74 (CHCl<sub>3</sub>–MeOH, 10:1), mp 160–161°C,  $[\alpha]_D^{24} = 49^\circ$  ( $c = 5.27$ , CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1250 (OCOCH<sub>3</sub>), 1670 (C=C–C=O), 1750 (OCOCH<sub>3</sub>). UV spectrum:  $\lambda_{max}$  240 nm ( $\epsilon = 11330$ ). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.73 s (3H, C<sup>18</sup>H<sub>3</sub>), 1.00 s (3H, C<sup>19</sup>H<sub>3</sub>), 1.14 s and 1.15 s (3H, C<sup>21</sup>H<sub>3</sub>), 1.31 s (~2H, C<sup>24</sup>=C<sup>25</sup>–C<sup>27</sup>H<sub>3</sub>), 1.39 s and 1.63 s (6H, Me<sub>2</sub>C), 1.70 s (~2H, C<sup>25</sup>=C<sup>24</sup>–C<sup>26</sup>H<sub>3</sub>), 1.73 s (~1H, C<sup>26</sup>=C<sup>25</sup>–C<sup>27</sup>H<sub>3</sub>), 1.75–2.12 m (~14.7H, CH<sub>2</sub>), 1.98 s and 2.09 s (6H, MeCO), 2.12–2.30 m (1H, 17-H), 2.35 d.d (1H, 5-H, <sup>3</sup>J = 5.0, 12.0 Hz), 3.09 m (1H, 9-H,  $\omega_{1/2} = 24.0$  Hz), 3.63–3.71 m (1H, 22-H), 4.70 br.s and 4.72 br.s (~0.7H, =C<sup>26</sup>H<sub>2</sub>,  $\omega_{1/2} = 5.0, 5.0$  Hz), 5.00–5.06 m (1H, 2-H), 5.16 t (~0.7H, =C<sup>24</sup>H, <sup>3</sup>J = 6.0 Hz), 5.31 br.s (1H, 3-H,  $\omega_{1/2} = 7.8$  Hz), 5.85 br.s (1H, 7-H,  $\omega_{1/2} = 6.7$  Hz). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 17.0 q (C<sup>18</sup> and C<sup>27</sup>–C<sup>25</sup>=C<sup>24</sup>), 18.0 q (C<sup>27</sup>–C<sup>25</sup>=C<sup>24</sup>), 20.3 t (C<sup>16</sup>), 21.0 q (MeCO), 21.0 t (C<sup>11</sup>), 22.6 q (C<sup>21</sup>), 23.7 q (C<sup>19</sup>), 25.6 q (C<sup>26</sup>–C<sup>25</sup>=C<sup>24</sup>), 26.7 t (C<sup>23</sup>), 26.8 q and 28.9 q (Me<sub>2</sub>C), 27.9 t (C<sup>15</sup>), 29.1 t (C<sup>12</sup>), 30.8 t (C<sup>4</sup>), 33.6 d (C<sup>9</sup>), 33.9 t (C<sup>1</sup>), 35.1 t (C<sup>24</sup>–C<sup>25</sup>=C<sup>26</sup>), 38.2 s (C<sup>10</sup>), 47.1 s (C<sup>13</sup>), 49.0 d (C<sup>17</sup>), 50.8 d (C<sup>5</sup>), 66.9 d (C<sup>3</sup>), 68.6 d (C<sup>2</sup>), 80.7 d and 80.9 d (C<sup>22</sup>), 84.0 s (C<sup>20</sup>), 84.5 s (C<sup>14</sup>), 106.7 s (Me<sub>2</sub>C), 109.9 t (C<sup>26</sup>=C<sup>25</sup>), 120.3 d (C<sup>7</sup>), 121.3 d (C<sup>24</sup>=C<sup>25</sup>), 133.6 s (C<sup>25</sup>=C<sup>24</sup>), 145.3 s (C<sup>25</sup>=C<sup>26</sup>), 164.9 s (C<sup>8</sup>), 170.2 s and 170.5 s (MeCO), 202.2 s (C<sup>6</sup>). Found, %: C 69.72; H 8.48. C<sub>34</sub>H<sub>50</sub>O<sub>8</sub>. Calculated, %: C 69.60; H 8.59.

**(20R,22R)-2 $\beta$ ,3 $\beta$ -Diacetoxy-14 $\alpha$ -hydroxy-20,22-isopropylidenedioxy-27-nor-5 $\beta$ -cholest-7-ene-6,25-dione (VIII) and (20R,22R)-2 $\beta$ ,3 $\beta$ -diacetoxy-14 $\alpha$ ,24-dihydroxy-20,22-isopropylidenedioxy-25,26,27-trinor-5 $\beta$ -cholest-7-en-6-one (IX).** An ozone–oxygen mixture was passed at a flow rate of 10 ml/min over a period of 1 min through a solution of 0.254 g (0.43 mmol) of compound **VII** ( $\Delta^{24}/\Delta^{25}$  isomer mixture) and 0.052 g (0.87 mmol) of glacial acetic acid in 2 ml of methylene chloride under vigorous stirring and cooling to –2°C (until 0.43 mmol of O<sub>3</sub> was absorbed). The mixture was purged with argon and was slowly added under stirring to a suspension of NaBH(OAc)<sub>3</sub> in methylene chloride [prepared by adding a solution of 0.355 g (5.9 mmol) of glacial acetic acid in 1 ml of methylene chloride to a suspension of 0.075 g (2.0 mmol) of NaBH<sub>4</sub> in 3 ml of methylene chloride, followed by stirring for 2 h], cooled to 10°C. The mixture was stirred for 3 h at 20°C, and a solution of 0.14 g of sodium hydroxide in 3 ml of water was added. The organic phase was washed with water (3×2 ml) and evaporated on a rotary evaporator, and

the residue was subjected to column chromatography on silica gel (10 g) using chloroform as eluent to isolate 0.09 g (35%) of ketone **VIII** ( $R_f$  0.75, CHCl<sub>3</sub>–MeOH, 10:1) and 0.11 g (45%) of alcohol **IX** ( $R_f$  0.44, CHCl<sub>3</sub>–MeOH, 10:1).

Compound **VIII**. mp 143–144°C,  $[\alpha]_D^{21} = 52.4^\circ$  ( $c = 5.3$ , CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1250 (OCOCH<sub>3</sub>); 1670, 1710 (C=C–C=O); 1720 (C=O); 1750 (OCOCH<sub>3</sub>). UV spectrum:  $\lambda_{max}$  241 nm ( $\epsilon = 9102$ ). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.77 s (3H, C<sup>18</sup>H<sub>3</sub>); 1.06 s (3H, C<sup>19</sup>H<sub>3</sub>); 1.14 s (3H, C<sup>21</sup>H<sub>3</sub>); 1.24 s, 1.29 s, and 1.43 s (6H, Me<sub>2</sub>C); 1.30–2.80 m (17H, CH, CH<sub>2</sub>); 2.03 s (3H, C<sup>26</sup>H<sub>3</sub>); 2.11 s and 2.16 s (6H, MeCO); 2.37 d.d (1H, 5-H, <sup>3</sup>J = 12.3, 5.0); 3.11 m (1H, 9-H,  $\omega_{1/2} = 22.2$  Hz); 3.59 m (1H, 22-H,  $\omega_{1/2} = 8.0$  Hz); 5.05 m (1H, 2-H,  $\omega_{1/2} = 21.0$  Hz); 5.34 m (1H, 3-H,  $\omega_{1/2} = 9.2$  Hz); 5.86 br.s (1H, 7-H,  $\omega_{1/2} = 8.0$  Hz). <sup>13</sup>C NMR spectrum,  $\delta_C$ , ppm: 17.0 q (C<sup>18</sup>), 18.8 t (C<sup>16</sup>), 20.3 t (C<sup>11</sup>), 21.0 q (MeCO), 21.9 q (C<sup>21</sup>), 23.8 q (C<sup>19</sup>), 26.8 q (C<sup>26</sup>), 28.9 q and 30.0 q (Me<sub>2</sub>C), 29.1 q (C<sup>23</sup>), 29.6 t (C<sup>15</sup>), 30.7 t (C<sup>12</sup>), 31.5 t (C<sup>4</sup>), 33.6 d (C<sup>9</sup>), 33.9 t (C<sup>24</sup>), 34.8 t (C<sup>1</sup>), 38.3 s (C<sup>10</sup>), 47.1 s (C<sup>13</sup>), 48.9 d (C<sup>17</sup>), 50.9 d (C<sup>5</sup>), 67.0 d (C<sup>3</sup>), 68.6 d (C<sup>2</sup>), 80.4 d (C<sup>22</sup>), 84.2 s (C<sup>20</sup>), 84.5 s (C<sup>14</sup>), 107.0 s (Me<sub>2</sub>C), 121.4 d (C<sup>7</sup>), 164.9 s (C<sup>8</sup>), 170.2 s and 170.5 s (MeCO), 202.3 s (C<sup>6</sup>), 208.5 s (C<sup>25</sup>). Found, %: C 67.48; H 8.13. C<sub>33</sub>H<sub>48</sub>O<sub>9</sub>. Calculated, %: C 67.32; H 8.22.

Compound **IX**. mp 144–146°C,  $[\alpha]_D^{23} = 42.5^\circ$  ( $c = 7.0$ , CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1250 (OCOCH<sub>3</sub>), 1670 (C=C–C=O), 1750 (OCOCH<sub>3</sub>). UV spectrum:  $\lambda_{max}$  243 nm ( $\epsilon = 12525$ ). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.78 s (3H, C<sup>18</sup>H<sub>3</sub>), 1.01 s (3H, C<sup>19</sup>H<sub>3</sub>), 1.14 s (3H, C<sup>21</sup>H<sub>3</sub>), 1.32 s and 1.39 s (6H, Me<sub>2</sub>C), 1.47–2.43 m (18H, CH, CH<sub>2</sub>), 1.99 s and 2.09 s (6H, MeCO), 3.09 m (1H, 9-H,  $\omega_{1/2} = 25.5$  Hz), 3.80 m (1H, 22-H), 5.03 m (1H, 2-H,  $\omega_{1/2} = 20.0$  Hz), 5.31 br.s (1H, 3-H,  $\omega_{1/2} = 12.2$  Hz), 5.85 br.s (1H, 7-H,  $\omega_{1/2} = 6.0$  Hz). <sup>13</sup>C NMR spectrum,  $\delta_C$ , ppm: 17.1 q (C<sup>18</sup>), 20.3 t (C<sup>16</sup>), 20.9 q and 21.0 q (MeCO), 21.0 t (C<sup>11</sup>), 22.0 q (C<sup>21</sup>), 23.8 q (C<sup>19</sup>), 26.9 q and 28.9 q (Me<sub>2</sub>C), 29.1 q (C<sup>23</sup>), 30.8 t (C<sup>15</sup>), 31.3 t (C<sup>12</sup>), 31.4 t (C<sup>4</sup>), 33.6 d (C<sup>9</sup>), 33.9 t (C<sup>1</sup>), 38.3 s (C<sup>10</sup>), 47.1 s (C<sup>13</sup>), 48.9 d (C<sup>17</sup>), 50.9 d (C<sup>5</sup>), 61.4 t (C<sup>24</sup>), 67.0 d (C<sup>3</sup>), 68.6 d (C<sup>2</sup>), 80.0 d (C<sup>22</sup>), 84.4 s (C<sup>20</sup>), 84.5 s (C<sup>14</sup>), 107.5 s (Me<sub>2</sub>C), 121.4 d (C<sup>7</sup>), 164.9 s (C<sup>8</sup>), 170.2 s and 170.5 s (MeCO), 202.3 s (C<sup>6</sup>). Found, %: C 66.22; H 8.15. C<sub>31</sub>H<sub>46</sub>O<sub>9</sub>. Calculated, %: C 66.17; H 8.24.

**(20R,22R)-2 $\beta$ ,3 $\beta$ -Diacetoxy-20,22-isopropylidenedioxy-14 $\alpha$ ,24-bis(trimethylsiloxy)-25,26,27-trinor-5 $\beta$ -cholest-7-en-6-one (X).** Tetrabutylammonium

fluoride, 0.3 mg (0.8 mol %), was added at 0°C under stirring to a mixture of 0.07 g (0.12 mmol) of compound **IX** and 0.106 g (0.75 mmol) of Me<sub>3</sub>SiCF<sub>3</sub> 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<sub>3</sub> as eluent to isolate 0.67 g (96%) of compound **X**, *R*<sub>f</sub> 0.78 (CHCl<sub>3</sub>-MeOH, 20:1), mp 57–59°C,  $[\alpha]_D^{20} = 41.7^\circ$  (*c* = 6.66, CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 840, 1250 (SiCH<sub>3</sub>); 1670 (C=C-C=O); 1730 (COCH<sub>3</sub>). UV spectrum:  $\lambda_{\max}$  241 nm ( $\epsilon = 13149$ ). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.09 s and 0.10 s (18H, Me<sub>3</sub>Si), 0.74 s (3H, C<sup>18</sup>H<sub>3</sub>), 1.02 s (3H, C<sup>19</sup>H<sub>3</sub>), 1.12 s (3H, C<sup>21</sup>H<sub>3</sub>), 1.31 s and 1.40 s (6H, Me<sub>2</sub>C), 1.48–2.32 m (17H, CH, CH<sub>2</sub>), 2.01 s and 2.10 s (6H, MeCO), 2.39 d.d (1H, 5-H, <sup>3</sup>*J* = 4.1, 13.3 Hz), 2.98 m (1H, 9-H), 3.60–3.83 m (1H, 22-H), 5.02 m (1H, 2-H), 5.37 br.s (1H, 3-H,  $\omega_{1/2} = 10.0$  Hz), 5.86 d (1H, 7-H, <sup>4</sup>*J* = 2.3 Hz). <sup>13</sup>C NMR spectrum,  $\delta_C$ , ppm: 0.6 q and 1.9 q (Me<sub>3</sub>Si), 16.2 q (C<sup>18</sup>), 20.4 t (C<sup>11</sup>), 20.9 q and 21.0 q (MeCO), 21.3 t (C<sup>16</sup>), 21.9 q (C<sup>21</sup>), 24.1 q (C<sup>19</sup>), 26.8 q and 28.9 q (Me<sub>2</sub>C), 29.2 q (C<sup>23</sup>), 29.7 t (C<sup>15</sup>), 29.7 t (C<sup>12</sup>), 31.0 t (C<sup>4</sup>), 32.5 t (C<sup>1</sup>), 33.9 d (C<sup>9</sup>), 38.3 s (C<sup>10</sup>), 48.6 s (C<sup>13</sup>), 48.9 d (C<sup>17</sup>), 50.9 d (C<sup>5</sup>), 59.8 t (C<sup>24</sup>), 67.0 d (C<sup>3</sup>), 68.6 d (C<sup>2</sup>), 77.5 d (C<sup>22</sup>), 84.0 s (C<sup>20</sup>), 87.7 s (C<sup>14</sup>), 107.0 s (Me<sub>2</sub>C), 122.1 d (C<sup>7</sup>), 164.1 s (C<sup>8</sup>), 170.1 s and 170.2 s (MeCO), 201.9 s (C<sup>6</sup>). Found, %: C 62.97; H 8.75. C<sub>37</sub>H<sub>62</sub>O<sub>9</sub>Si<sub>2</sub>. Calculated, %: C 62.85; H 8.84.

**(20R,22R,25RS)-2 $\beta$ ,3 $\beta$ -Diacetoxy-20,22-isopropylidenedioxy-25-trifluoromethyl-14 $\alpha$ ,25-bis(trimethylsiloxy)-27-nor-5 $\beta$ -cholest-7-en-6-one (XI).** Tetrabutylammonium fluoride, 0.2 mg (0.8 mol %), was added at 0°C under stirring to a mixture of 0.041 g (0.07 mmol) of compound **VIII** and 0.03 g (0.21 mmol) of Me<sub>3</sub>SiCF<sub>3</sub> 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 chloroform as eluent to isolate 0.04 g (87%) of compound **XI**, *R*<sub>f</sub> 0.77 (CHCl<sub>3</sub>-MeOH, 20:1), mp 52–54°C,  $[\alpha]_D^{24} = 38.6^\circ$  (*c* = 4.6, CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 830 (SiCH<sub>3</sub>), 1160 (CF<sub>3</sub>), 1245 (SiCH<sub>3</sub>), 1245 (OCOCH<sub>3</sub>), 1360 (CF<sub>3</sub>), 1670 (C=C-C=O), 1730 (COCH<sub>3</sub>). UV spectrum:  $\lambda_{\max}$  240 nm ( $\epsilon = 11050$ ). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.08 s, 0.09 s, 0.17 s, and 0.23 s (18H, Me<sub>3</sub>Si); 0.75 s (3H, C<sup>18</sup>H<sub>3</sub>); 1.13 s (3H, C<sup>19</sup>H<sub>3</sub>); 1.15 s (3H, C<sup>21</sup>H<sub>3</sub>); 1.25 s and 1.38 s (3H, C<sup>26</sup>H<sub>3</sub>); 1.31 s and 1.40 s (6H, Me<sub>2</sub>C); 2.12 s and 2.18 s (6H, MeCO); 1.40–2.60 m

(18H, CH, CH<sub>2</sub>); 2.92 m (1H, 9-H,  $\omega_{1/2} = 35.0$  Hz); 3.63 m (1H, 22-H,  $\omega_{1/2} = 19.0$  Hz); 5.26 m (1H, 2-H,  $\omega_{1/2} = 12.5$  Hz); 5.38 m (1H, 3-H,  $\omega_{1/2} = 9.0$  Hz); 5.86 br.s (1H, 7-H,  $\omega_{1/2} = 10.0$  Hz). <sup>13</sup>C NMR spectrum,  $\delta_C$ , ppm: 1.6 q, 2.0 q, and 2.1 q (Me<sub>3</sub>Si); 16.3 q (C<sup>18</sup>); 20.3 q (C<sup>19</sup>); 21.1 q and 21.2 q (MeCO); 21.5 t (C<sup>11</sup>); 22.0 q (C<sup>21</sup>); 24.2 q and 26.8 q (C<sup>26</sup>); 26.4 t (C<sup>16</sup>); 26.9 q and 29.0 q (Me<sub>2</sub>C); 29.7 t (C<sup>23</sup>); 29.9 t (C<sup>12</sup> and C<sup>15</sup>); 31.1 t (C<sup>4</sup>); 33.2 t (C<sup>24</sup>); 34.1 d (C<sup>9</sup>); 35.5 t (C<sup>1</sup>); 38.4 s (C<sup>10</sup>); 48.8 s (C<sup>13</sup>); 49.2 d (C<sup>17</sup>); 50.9 d (C<sup>5</sup>); 68.6 d (C<sup>3</sup>); 69.4 d (C<sup>2</sup>); 76.2 q (C<sup>25</sup>, <sup>2</sup>*J*<sub>CF</sub> = 28 Hz); 81.3 d (C<sup>22</sup>); 84.2 s (C<sup>20</sup>); 87.7 s (C<sup>14</sup>); 106.9 s (Me<sub>2</sub>C); 122.3 d (C<sup>7</sup>); 126.7 q (C<sup>27</sup>F<sub>3</sub>, <sup>1</sup>*J*<sub>CF</sub> = 298 Hz); 164.2 s (C<sup>8</sup>); 170.2 s (MeCO); 202.3 s (C<sup>6</sup>). Found, %: C 59.93; H 8.09. C<sub>40</sub>H<sub>65</sub>F<sub>3</sub>O<sub>9</sub>Si<sub>2</sub>. Calculated, %: C 59.82; H 8.16.

**(20R,22R,25RS)-2 $\beta$ ,3 $\beta$ -Dihydroxy-20,22-isopropylidenedioxy-25-trifluoromethyl-14 $\alpha$ ,25-bis(trimethylsiloxy)-27-nor-5 $\beta$ -cholest-7-en-6-one (XII).** Compound **XI**, 0.136 g (0.17 mmol), was dissolved in a mixture of 2 ml of methanol and 1 ml of chloroform, and 1 ml of a 20% solution of sodium hydroxide was added under stirring. When the reaction was complete (TLC), the solvent was distilled off, 5 ml of water was added to the residue, and the mixture was extracted with diethyl ether (3×10 ml). The extract was washed with water (3 ml), dried over MgSO<sub>4</sub>, and evaporated under reduced pressure to obtain 0.118 g (97%) of compound **XII**, *R*<sub>f</sub> 0.4 (CHCl<sub>3</sub>-MeOH, 20:1), mp 110–112°C,  $[\alpha]_D^{20} = 36.9^\circ$  (*c* = 2.92, CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 850 (SiCH<sub>3</sub>), 1145 (CF<sub>3</sub>), 1245 (SiCH<sub>3</sub>), 1350 (CF<sub>3</sub>), 1665 (C=C-C=O). UV spectrum:  $\lambda_{\max}$  240 nm ( $\epsilon = 10250$ ). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.06 s, 0.07 s, 0.11 s, and 0.16 s (18H, Me<sub>3</sub>Si); 0.74 s (3H, C<sup>18</sup>H<sub>3</sub>); 1.12 s (3H, C<sup>19</sup>H<sub>3</sub>); 1.15 s (3H, C<sup>21</sup>H<sub>3</sub>); 1.25 s and 1.37 s (3H, C<sup>26</sup>H<sub>3</sub>); 1.31 s and 1.40 s (6H, Me<sub>2</sub>C); 1.50–2.60 m (18H, CH, CH<sub>2</sub>); 2.91 m (1H, 9-H,  $\omega_{1/2} = 30.0$  Hz); 3.63 m (1H, 22-H,  $\omega_{1/2} = 20.0$  Hz); 3.84 m (1H, 2-H,  $\omega_{1/2} = 23.5$  Hz); 4.08 m (1H, 3-H,  $\omega_{1/2} = 18.0$  Hz); 5.83 br.s (1H, 7-H,  $\omega_{1/2} = 12.8$  Hz). <sup>13</sup>C NMR spectrum,  $\delta_C$ , ppm: 1.8 q and 2.0 q (Me<sub>3</sub>Si), 16.2 q (C<sup>18</sup>), 20.2 q (C<sup>21</sup>), 20.4 t (C<sup>11</sup>), 21.0 q and 24.2 q (C<sup>26</sup>), 21.2 t (C<sup>16</sup>), 21.4 q (C<sup>19</sup>), 26.3 t (C<sup>23</sup>), 26.8 q and 28.9 q (Me<sub>2</sub>C), 29.6 t (C<sup>15</sup>), 29.8 t (C<sup>12</sup>), 31.0 t (C<sup>4</sup>), 33.1 t (C<sup>24</sup>), 33.5 d (C<sup>9</sup>), 34.4 t (C<sup>1</sup>), 38.1 s (C<sup>10</sup>), 48.8 s (C<sup>13</sup>), 49.1 d (C<sup>17</sup>), 49.3 d (C<sup>5</sup>), 67.3 d (C<sup>3</sup>), 68.0 d (C<sup>2</sup>), 73.1 q (C<sup>25</sup>, <sup>2</sup>*J*<sub>CF</sub> = 28 Hz), 81.2 d (C<sup>22</sup>), 84.2 s (C<sup>20</sup>), 87.7 s (C<sup>14</sup>), 106.9 s (Me<sub>2</sub>C), 122.3 d (C<sup>7</sup>), 126.4 q (C<sup>27</sup>, <sup>1</sup>*J*<sub>CF</sub> = 284 Hz), 163.9 s (C<sup>8</sup>), 203.6 s (C<sup>6</sup>). Found, %: C 60.28; H 8.42. C<sub>36</sub>H<sub>61</sub>F<sub>3</sub>O<sub>7</sub>Si<sub>2</sub>. Calculated, %: C 60.14; H 8.55.



**(20R,22R,25RS)-2 $\beta$ ,3 $\beta$ ,14 $\alpha$ ,25-Tetrahydroxy-20,22-isopropylidenedioxy-25-trifluoromethyl-27-nor-5 $\beta$ -cholest-7-en-6-one (XIII).** *a.* A mixture of 0.10 g (0.14 mmol) of compound **XII**, 0.17 g of tetrabutylammonium fluoride, one drop of water, one drop of 5% hydrochloric acid, and 2 ml of THF was stirred for 4 h. Ethyl acetate, 5 ml, was then added, and the mixture was washed with 3 ml of water, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel (10 g) using CHCl<sub>3</sub>–MeOH (5:1) as eluent to isolate 0.05 g (80%) of compound **XIII**, *R<sub>f</sub>* 0.58, mp 123–125°C, [ $\alpha$ ]<sub>D</sub><sup>24</sup> = 24.1° (*c* = 2.59, CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1150, 1360 (CF<sub>3</sub>); 1650 (C=C–C=O). UV spectrum:  $\lambda_{\max}$  243 nm ( $\epsilon$  = 11450). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.78 s (3H, C<sup>18</sup>H<sub>3</sub>), 0.95 s (3H, C<sup>19</sup>H<sub>3</sub>), 1.16 s (3H, C<sup>21</sup>H<sub>3</sub>), 1.26 s and 1.33 s (3H, C<sup>26</sup>H<sub>3</sub>), 1.34 s and 1.42 s (6H, Me<sub>2</sub>C), 1.50–2.50 m (18H, CH, CH<sub>2</sub>), 3.02 m (1H, 9-H,  $\omega_{1/2}$  = 27.0 Hz), 3.65 m (1H, 22-H,  $\omega_{1/2}$  = 27.0 Hz), 3.86 m (1H, 2-H,  $\omega_{1/2}$  = 30.0 Hz), 4.01 m (1H, 3-H,  $\omega_{1/2}$  = 17.0 Hz), 5.84 br.s (1H, 7-H,  $\omega_{1/2}$  = 12.8 Hz). <sup>13</sup>C NMR spectrum,  $\delta$ <sub>C</sub>, ppm: 13.6 q (C<sup>18</sup>), 17.0 q (C<sup>19</sup>), 19.7 t (C<sup>11</sup>), 20.0 q and 23.9 q (C<sup>26</sup>), 21.1 t (C<sup>16</sup>), 21.9 q (C<sup>21</sup>), 23.9 t (C<sup>23</sup>), 26.8 q and 28.9 q (Me<sub>2</sub>C), 29.7 t (C<sup>12</sup>), 31.1 t (C<sup>15</sup>), 31.2 t (C<sup>4</sup>), 32.9 t (C<sup>24</sup>), 33.8 d (C<sup>9</sup>), 36.5 t (C<sup>1</sup>), 38.1 s (C<sup>10</sup>), 47.3 s (C<sup>13</sup>), 49.0 d (C<sup>17</sup>), 50.1 d (C<sup>5</sup>), 67.5 d (C<sup>3</sup>), 67.6 d (C<sup>2</sup>), 73.3 q (C<sup>25</sup>, <sup>2</sup>*J*<sub>CF</sub> = 28 Hz), 81.6 d (C<sup>22</sup>), 84.3 s (C<sup>20</sup>), 84.9 s (C<sup>14</sup>), 107.2 s (Me<sub>2</sub>C), 121.4 d (C<sup>7</sup>), 125.9 q (C<sup>27</sup>F<sub>3</sub>, <sup>1</sup>*J*<sub>CF</sub> = 286 Hz), 165.5 s (C<sup>8</sup>), 204.9 s (C<sup>6</sup>). Found, %: C 62.83; H 7.72. C<sub>30</sub>H<sub>45</sub>F<sub>3</sub>O<sub>7</sub>. Calculated, %: C 62.70; H 7.89.

*b.* A mixture of 0.016 g (0.03 mmol) of compound **XVI** and 1 ml of 70% acetic acid was stirred for 1.5 h. The mixture was diluted with 5 ml of water and extracted with 1-butanol (3×3 ml), the extract was washed with water (2 ml) and evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (5 g) using CHCl<sub>3</sub>–MeOH (10:1) as eluent. Yield of **XIII** 0.012 g (82%); the product was identical to a sample prepared as described above in *a*.

**(20R,22R,25RS)-2 $\beta$ ,3 $\beta$ :20,22-Bis(isopropylidenedioxy)-6 $\alpha$ ,25-bis(trifluoromethyl)-6 $\beta$ ,14 $\alpha$ ,25-tris(trimethylsiloxy)-27-nor-5 $\beta$ -cholest-7-en-6-one (XV) and (20R,22R,25RS)-14 $\alpha$ ,25-dihydroxy-2 $\beta$ ,3 $\beta$ :20,22-bis(isopropylidenedioxy)-25-trifluoromethyl-27-nor-5 $\beta$ -cholest-7-en-6-one (XVI).** Tetrabutylammonium fluoride, 0.3 mg (0.8 mol %), was added at 0°C under stirring to a mixture of 0.1 g (0.16 mmol) of diketone **V** and 0.138 g (0.97 mmol) of Me<sub>3</sub>SiCF<sub>3</sub> 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<sub>3</sub> as eluent to isolate 0.089 g of a ~1:1 mixture of compounds **XIV** and **XV**. Repeated chromatography on silica gel (5 g) with CHCl<sub>3</sub> as eluent afforded 0.021 g (14%) of compound **XV**, *R<sub>f</sub>* 0.74 (CHCl<sub>3</sub>–MeOH, 20:1) and 0.06 g of a mixture of **XIV** and **XV** at a ratio of 2:1 (according to the 7-H signal intensity ratio in the <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub>,  $\delta$  5.8 and 5.4 ppm, respectively). This mixture, 0.06 g, and 0.17 g of Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup> were dissolved in 2 ml of THF, the solution was stirred for 4 h, 3 ml of ethyl acetate was added, and the resulting mixture was washed with 2 ml of water, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel (5 g) using CHCl<sub>3</sub>–MeOH (20:1) as eluent. We thus isolated 0.02 g (20%, calculated on initial compound **V**) of compound **XVI**, *R<sub>f</sub>* 0.37 (CHCl<sub>3</sub>–MeOH, 10:1).

Compound **XV**. mp 57–59°C, [ $\alpha$ ]<sub>D</sub><sup>18</sup> = 97.2° (*c* = 1.08, CHCl<sub>3</sub>). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 840 (SiCH<sub>3</sub>), 1155 (CF<sub>3</sub>), 1250 (SiCH<sub>3</sub>), 1370 (CF<sub>3</sub>). UV spectrum:  $\lambda_{\max}$  231 nm ( $\epsilon$  = 1198). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.12 s (9H, Me<sub>3</sub>Si); 0.18 s (18H, Me<sub>3</sub>Si); 0.25 s (3H, C<sup>19</sup>H<sub>3</sub>); 0.68 s (3H, C<sup>18</sup>H<sub>3</sub>); 1.11 s (3H, C<sup>21</sup>H<sub>3</sub>); 1.22 s and 1.26 s (3H, C<sup>26</sup>H<sub>3</sub>); 1.31 s, 1.39 s, 1.40 s, and 1.52 s (12H, Me<sub>2</sub>C); 1.09–2.22 m (18H, CH, CH<sub>2</sub>); 2.29 d.d (1H, 5-H, <sup>3</sup>*J* = 4.0, 13.0 Hz); 2.48 d.d (1H, 17-H, <sup>3</sup>*J* = 7.4, 14.0 Hz); 3.63 m (2H, 9-H, 22-H,  $\omega_{1/2}$  = 15.3 Hz); 4.34 t (1H, 3-H, <sup>3</sup>*J* = 6.3 Hz); 4.58 d.d (1H, 2-H, <sup>3</sup>*J* = 9.0, 15.0 Hz); 5.40 br.s (1H, 7-H,  $\omega_{1/2}$  = 4.0 Hz). <sup>13</sup>C NMR spectrum,  $\delta$ <sub>C</sub>, ppm: 1.8 q, 1.9 q, 2.0 q, and 2.1 q (Me<sub>3</sub>Si); 16.3 q (C<sup>18</sup>); 20.8 q (C<sup>19</sup>); 21.7 q (C<sup>21</sup>); 22.0 t (C<sup>11</sup>); 22.4 t (C<sup>16</sup>); 24.3 t (C<sup>23</sup>); 24.3 q, 27.5 q, and 29.0 q (Me<sub>2</sub>C); 24.9 q and 26.8 q (C<sup>26</sup>); 27.4 t (C<sup>15</sup>); 28.2 t (C<sup>12</sup>); 29.7 t (C<sup>4</sup>); 32.3 s (C<sup>10</sup>); 33.3 t (C<sup>1</sup>); 35.7 t (C<sup>24</sup>); 39.2 d (C<sup>9</sup>); 44.2 d (C<sup>5</sup>); 49.4 d (C<sup>17</sup>); 52.0 s (C<sup>13</sup>); 71.4 d (C<sup>3</sup>); 73.1 d (C<sup>2</sup>); 75.8 q (C<sup>6</sup>, <sup>2</sup>*J*<sub>CF</sub> = 26.0 Hz); 75.9 q (C<sup>25</sup>, <sup>2</sup>*J*<sub>CF</sub> = 28.0 Hz); 81.3 d (C<sup>22</sup>); 84.3 s (C<sup>20</sup>); 89.6 s (C<sup>14</sup>); 106.7 s (20,22-*O*-Me<sub>2</sub>C); 106.8 s (2,3-*O*-Me<sub>2</sub>C); 113.9 d (C<sup>7</sup>); 126.3 q (CF<sub>3</sub>, <sup>1</sup>*J*<sub>CF</sub> = 286.0 Hz); 147.8 s (C<sup>8</sup>). Mass spectrum (CI), *m/z* (*I*<sub>rel</sub>, %): reactant gas NH<sub>3</sub>: 918 (16.2) [*M* + NH<sub>4</sub>]<sup>+</sup>, 901 (3) [*M* + H]<sup>+</sup>, 862 (45.4), 843 (55.6) [*M* + H – C<sub>3</sub>H<sub>6</sub>O]<sup>+</sup>, 828 (100) [*M* + H – Me<sub>3</sub>Si]<sup>+</sup>, 812 (20.5), 785 (13.4), 771 (20.2), 753 (27.1), 738 (83), 721 (63.6), 700 (15.5), 663 (10.9), 646 (10.1), 573 (7.4), 346 (13.6), 327 (67.4), 284 (11.6), 124 (1.2); reactant gas CH<sub>4</sub>: 916 (19.1)

$[M + CH_4]^+$ , 901 (3.1)  $[M]^+$ , 883 (59.7), 842 (60)  $[M - C_3H_6O]^+$ , 827 (100)  $[M - Me_3Si]^+$ , 812 (34.7), 753 (64.1), 738 (34.4), 731 (37.2), 573 (55.6), 483 (26.9), 327 (36.9), 284 (59.4), 154 (13.8). Found, %: C 57.38; H 8.12.  $C_{43}H_{74}F_6O_7Si_3$ . Calculated, %: C 57.30; H 8.28.

Compound **XVI**. mp 98–102°C. IR spectrum,  $\nu$ ,  $cm^{-1}$ : 1150, 1350 ( $CF_3$ ); 1650 ( $C=C-C=O$ ). UV spectrum:  $\lambda_{max}$  242 nm ( $\epsilon = 11470$ ).  $^1H$  NMR spectrum,  $\delta$ , ppm: 0.81 s (3H,  $C^{18}H_3$ ); 1.03 s (3H,  $C^{19}H_3$ ); 1.26 s (3H,  $C^{21}H_3$ ); 1.38 s and 1.52 s (3H,  $C^{26}H_3$ ); 1.33 s, 1.34 s, 1.43 s, and 1.50 s (12H,  $Me_2C$ ); 1.50–2.50 m (18H, CH,  $CH_2$ ); 3.60–3.80 m (2H, 9-H, 22-H); 4.34 m (1H, 3-H,  $\omega_{1/2} = 13.0$  Hz); 4.58 m (1H, 2-H,  $\omega_{1/2} = 26.0$  Hz); 5.40 br.s (1H, 7-H,  $\omega_{1/2} = 4.5$  Hz).  $^{13}C$  NMR spectrum,  $\delta_C$ , ppm: 17.4 q ( $C^{18}$ ); 21.0 q ( $C^{19}$ ); 21.2 t ( $C^{11}$ ); 21.9 t ( $C^{16}$ ); 22.4 q ( $C^{21}$ ); 24.9 t ( $C^{23}$ ); 26.3 q, 26.9 q, 28.5 q, and 28.9 q ( $Me_2C$ ); 27.8 q and 30.6 q ( $C^{26}$ ); 31.9 t ( $C^{12}$ ); 33.1 t ( $C^4$ ); 33.4 t ( $C^{15}$ ); 36.7 t ( $C^{24}$ ); 38.0 d ( $C^9$ ); 40.0 t ( $C^1$ ); 41.8 s ( $C^{10}$ ); 47.7 s ( $C^{13}$ ); 48.8 d ( $C^{17}$ ); 50.5 d ( $C^5$ ); 75.8 q ( $C^{25}$ ,  $^2J_{CF} = 26.0$  Hz); 73.6 d ( $C^3$ ); 74.6 d ( $C^2$ ); 81.5 d ( $C^{22}$ ); 84.3 s ( $C^{20}$ ); 87.4 s ( $C^{14}$ ); 107.4 s (20,22-*O*- $Me_2C$ ); 107.5 s (2,3-*O*- $Me_2C$ ); 133.3 q ( $C^{27}F_3$ ,  $^1J_{CF} = 270.0$  Hz); 123.1 d ( $C^7$ ); 157.9 s ( $C^8$ ); 203.4 s ( $C^6$ ). Found, %: C 64.59; H 7.91.  $C_{33}H_{49}F_3O_7$ . Calculated, %: C 64.48; H 8.03.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 04-03-33103). The authors are also grateful to Prof. R.D. Lafont (Ecole Normale Supérieure, Laboratoire de Biochimie, CNRS-EP 119, 46 rue d'Ulm, F-75230 Paris Cedex 05, France) for recording the chemical ionization mass spectra.

## REFERENCES

1. Odinokov, V.N., Savchenko, R.G., Nazmeeva, S.R., Galyautdinov, I.V., and Khalilov, L.M., *Russ. J. Org. Chem.*, 2002, vol. 38, p. 525.
2. *Biomedical Frontiers of Fluorine Chemistry*, Qjima, I., McCarthy, J.R., and Welch, J.T., Eds., Washington DC: Am. Chem. Soc., 1996, ACS Symposium Series, vol. 639.
3. *Enantiocontrolled Synthesis of Organofluorine Compounds: Stereochemical Challenge and Biochemical Targets*, Sholoshonok, V.A., Ed., New York: Wiley, 1999.
4. Olah, G.A., Prakash, G.K.S., and Chambers, R.D., *Synthetic Fluorine Chemistry*, New York: Wiley, 1992.
5. Prakash, G.K.S. and Yudin, A.K., *Chem. Rev.*, 1997, vol. 97, p. 757.
6. Singh, R.P. and Shreeve, J.M., *Tetrahedron*, 2000, vol. 56, p. 7613.
7. Ishmuratov, G.Yu., Kharisov, R.Ya., Yakovleva, M.P., Botsman, O.V., Muslukhov, R.R., and Tolstikov, G.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1999, p. 198.
8. Pokrovskaya, I.E., Menyailo, A.T., Pospelov, M.V., Ryzhankova, A.K., Shil'nikova, A.G., Dubnik, G.N., and Mishina, L.S., *Neftekhimiya*, 1970, vol. 4, p. 554.
9. Odinokov, V.N., Savchenko, R.G., Nazmeeva, S.R., Galyautdinov, I.V., and Khalilov, L.M., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2002, p. 1784.
10. Odinokov, V.N., Akhmetova, V.R., Khasanov, Kh.D., Abduvakhobov, A.A., Khalilov, L.M., Cheskis, B.A., Moiseenkov, A.M., and Tolstikov, G.A., *Zh. Org. Khim.*, 1992, vol. 28, p. 1163.
11. Odinokov, V.N., Savchenko, R.G., Nazmeeva, S.R., and Galyautdinov, I.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2002, p. 1810.
12. Suksamrarn, A. and Pattanaprateen, P., *Tetrahedron*, 1995, vol. 51, p. 10 633.