Trifluoroacetylation and dehydration of 20-hydroxyecdysone acetonides. Synthesis of stachisterone B

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Trifluoroacetylation of the 25(OH)-group with subsequent dehydration of the 14(OH)-group takes place in the reaction of 20-hydroxyecdysone 20,22-acetonide and 2,3:20,22-diacetonide with trifluoroacetic anhydride in the presence of pyridine. Dehydration of the 14(OH)-group gives rise to stachisterone B derivatives, which are hydrolyzed to give the phytoecdysteroid stachisterone B.

Key words: 20-hydroxyecdysone, stachisterone B, acetonides, trifluoroacetates, dehydration, hydrolysis.

Ecdysteroids, which are insect and crustaceous hormones, are important as molting and metamorphosis regulators. These natural compounds are frequently encountered in the vegetable kingdom and, as these compounds are nontoxic, they are promising agents for medicine and agriculture.[1] Chemical transformations of readily available phytoecdysteroids represent the most efficient pathway to other phyto- and zooecdysteroids and their analogs seldom encountered in nature.[1,2]

We studied the transformations of 20,22-acetonide (**2**) and 2,3:20,22-diacetonide (**3**) of a widely distributed phytoecdysteroid, 20-hydroxyecdysone (**1**),[1,3] taking place on treatment with trifluoroacetic anhydride (TFAA). Before our communication dealing with dehydration of **1** to give the 20*S*-analog of shidasterone,[4] no examples of using TFAA in the ecdysteroid chemistry were reported.

It was found that treatment of compounds **2*** and **3** with 2 equiv. of TFAA in the presence of pyridine gives 25-trifluoroacetates **4** and **5**, respectively. The use of a smaller amount of TFAA results in a lower degree of conversion of **2** and **3**. The formation of **4** and **5** was confirmed by the data of their IR, ^{1}H NMR, and ^{13}C NMR spectra. Indeed, the IR spectra exhibit an absorption band at about 1770 cm^{-1} for the carbonyl group, and the ^{13}C NMR signal corresponding to the C(25) atom is substantially shifted downfield ($\Delta\delta \cong 19$) relative to the corresponding signal for the initial **2** and **3** (Table 1). The presence of the $COCF_3$ group in compounds **4** and **5** is also indicated by quartets in the region of δ 114 ($^1J_{CF} \cong$ 285 Hz) and δ 155—156 ($^2J_{CF} \cong 41$ Hz), due to its CF_3 and CO fragments. Whereas the formation of 25-trifluoroacetate **5** from diacetonide **3** was to be expected, the synthesis of 25-trifluoroacetate **4** from monoacetonide **2** is nontrivial, because acetylation of **2** with Ac_2O—Py in $CHCl_3$ is known[5] to involve first the C(2)OH and C(3)OH groups.

When the amount of TFAA is increased to 3 equiv., trifluoroacetylation is accompanied by dehydration of acetonides **2** and **3** involving the C(14)OH group to give 25-*O*-trifluoroacetyl-14,15-anhydro-20-hydroxyecdysone 20,22-acetonide (**6**) and 2,3:20,22-diacetonide (**7**), respectively. Compounds **6** and **7** can also be prepared by treating trifluoroacetates **4** and **5** with an equimolar amount of TFAA. The formation of the Δ^{14}-bond is confirmed unambiguously by typical olefinic-carbon signals at δ 130 (doublet for C(15)) and δ 150 (singlet at C(14)) observed in the J-modulated spin echo (JMOD) ^{13}C NMR spectra of compounds **6** and **7**; simultaneously, the ^{1}H NMR spectra of these compounds exhibit two one-proton signals in the region of δ 5.9—6.0 due to the H(7) and H(15) olefinic protons.

Hydrolysis of the 25-trifluoroacetate groups in monoacetonide **6** and diacetonide **7** on treatment with $NaHCO_3$ in a 80% aqueous solution of MeOH afforded monoacetonide **8** and diacetonide **9**, respectively. Acid hydrolysis of both products led to stachisterone B (**10**), identical (IR, UV, ^{1}H NMR) to the product isolated previously[1,6] in the amorphous state from the bark of the plant *Stachyurus praecox*.

* Monoacetonide **2** was prepared by the reaction between **1** and Me_2CO in the presence of HBF_4 (*cf.* Ref. 5).

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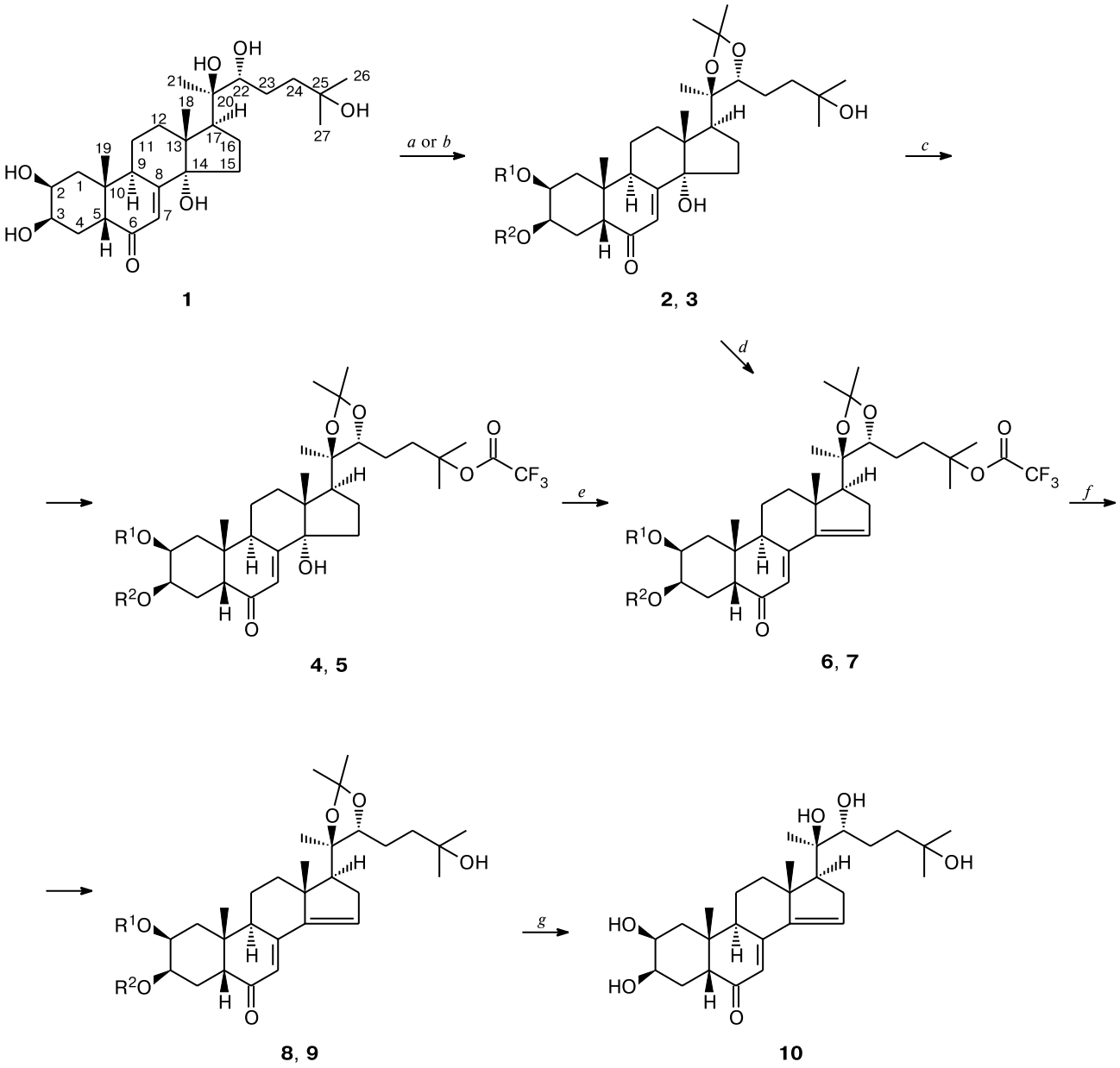
Scheme 1



a. Me_2CO/HBF_4. *b*. Me_2CO/phosphomolybdic acid. *c*. 2 equiv. TFAA/Py, $CHCl_3$. *d*. 3 equiv. TFAA/Py, $CHCl_3$. *e*. 1 equiv. TFAA/Py, $CHCl_3$. *f*. $NaHCO_3/MeOH—H_2O$, 8 : 2. *g*. 70% AcOH (aq.), $ZnCl_2$.

The structures of compounds **8**—**10** follow unambiguously from the ^1H and ^{13}C NMR spectra. It should be noted that the ^1H NMR spectrum of stachisterone recorded in C_5D_5N exhibits separate signals for H(7) and H(15) (as reported previously[1,6]), whereas in the spectrum recorded in CD_3OD, both protons are responsible for one signal at about δ 6.06.

Thus, stachisterone B (Scheme 1) was synthesized for the first time by the reaction of 20-hydroxyecdysone acetonides with TFAA—Py followed by hydrolysis.

Experimental

IR spectra were recorded on a Specord 75-IR spectrometer (in KBr pellets). UV spectra were measured on a Specord M-40 spectrometer for solutions in MeOH and $CHCl_3$. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-300 spectrom-

Table 1. Parameters of the ^{13}C NMR spectra (δ, *J*/Hz) of compounds **2**—**10** [a]

Atom	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
C(1)	37.7	37.5	36.4	38.2	38.1	38.0	39.4	37.5	39.9
C(2)	67.9	72.0	67.5	72.9	67.7	72.0	68.6	72.0	68.6
C(3)	67.8	71.5	67.3	71.6	67.2	71.6	68.6	72.6	68.6
C(4)	32.2	31.3	31.2	31.6	31.6	31.5	32.8	31.5	32.9
C(5)	51.1	50.7	49.9	50.8	49.7	50.7	51.5	50.6	51.5
C(6)	203.3	203.0	204.7	203.1	203.6	202.1	206.1	202.1	205.8
C(7)	121.5	121.2	121.1	121.3	120.6	120.7	121.1	120.6	121.2
C(8)	165.4	163.7	166.1	164.0	155.6	153.6	158.9	153.7	158.8
C(9)	34.2	34.3	33.7	34.5	38.4	38.5	39.8	38.6	39.8
C(10)	38.4	37.7	38.1	37.8	38.5	38.3	40.0	38.3	41.2
C(11)	20.8	20.4	20.2	20.6	20.5	20.4	22.3	20.5	21.7
C(12)	31.4	30.8	30.8	31.0	26.7	26.7	27.3	26.8	27.3
C(13)	47.6	47.2	47.1	47.5	47.5	47.5	[b]	47.5	[b]
C(14)	85.1	84.7	84.3	84.7	148.9	148.6	150.4	148.7	150.7
C(15)	31.5	26.5	27.6	26.7	128.4	128.0	130.2	128.1	130.3
C(16)	21.9	21.1	21.1	21.2	36.4	37.5	36.9	39.5	37.2
C(17)	49.7	48.9	49.1	49.2	57.7	57.7	58.8	57.5	59.1
C(18)	17.1	16.9	16.9	17.1	19.0	19.0	19.9	19.0	20.1
C(19)	24.2	23.4	23.7	23.6	23.2	23.2	24.1	23.2	24.0
C(20)	83.9	84.3	84.1	84.2	83.0	83.0	84.8	83.3	77.2
C(21)	22.2	21.8	21.8	21.9	21.1	21.1	24.1	21.1	24.0
C(22)	82.3	81.9	80.9	81.2	80.8	80.8	83.1	81.6	78.6
C(23)	24.1	23.5	23.0	23.1	23.1	23.1	25.1	23.6	27.3
C(24)	41.9	41.3	35.0	37.6	39.5	39.5	42.0	41.1	42.3
C(25)	69.1	70.3	88.8	88.9	88.7	88.6	71.3	70.2	71.3
C(26)	29.3	26.5	25.5	25.2	25.8	25.0	29.3	26.3	29.0
C(27)	29.3	26.8	25.1	25.8	25.0	25.8	29.0	26.7	29.9
2,3-$\underline{C}Me_2$		108.2		108.4		108.6		108.2	
2,3-$C\underline{Me}_2$		28.9, 29.3		28.5, 29.0		28.4, 28.8		29.2, 29.4	
20,22-$\underline{C}Me_2$	106.7	106.9	106.9	107.1	107.1	107.0	108.2	107.0	
20,22-$C\underline{Me}_2$	29.7, 29.9	28.4, 28.4	26.7, 27.6	26.5, 27.0	26.7, 28.8	26.3, 26.7	29.3, 29.7	28.5, 28.8	
$\underline{C}F_3CO_2$			114.3 ($^1J_{C,F}$ = 285.3)	114.4 ($^1J_{C,F}$ = 286.5)	114.3 ($^1J_{C,F}$ = 286.0)	114.3 ($^1J_{C,F}$ = 286.0)			
$CF_3\underline{C}O_2$			156.0 ($^2J_{C,F}$ = 41.0)	155.3 ($^2J_{C,F}$ = 41.4)	156.0 ($^2J_{C,F}$ = 41.4)	156.0 ($^2J_{C,F}$ = 41.0)			

[a] The spectra were recorded in $CDCl_3$ (**2**—**7**, **9**) and CD_3OD (**8**, **10**).
[b] The signals overlap with the signal of CD_3OD.

eters (operating at 300.13 MHz for ^1H and at 75 MHz for ^{13}C) for solutions in $CDCl_3$, CD_3OD, and C_5D_5N. Chemical shifts are given in the δ scale and referred to Me_4Si (internal standard). The specific rotation (deg mL g^{-1} dm^{-1}) was measured on a Perkin—Elmer-141 polarimeter; the concentrations are given in g·(100 mL)$^{-1}$. Melting points were determined on a Boetius hot stage. The following commercial chemicals were used: TFAA (Sigma), extra pure grade pyridine (kept for two weeks over solid KOH and distilled), analytical grade chloroform (GOST 3160-51), glacial AcOH (GOST 61-69), analytical grade Ac_2O (GOST 5815-69), analytical grade acetone (GOST 2603-63) (distilled), HBF_4 (TU 6-09-2577-77), and phosphomolybdic acid (TU 6-09-3540-78).

^{13}C NMR spectra of compounds **2**—**10** are presented in Table 1.

20-Hydroxyecdysone 20,22-acetonide, or (20*R*,22*R*)-2β,3β,14α,25-tetrahydroxy-20,22-isopropylidenedioxy-5β-cholest-7-en-6-one (2). HBF_4 (1 mL) was added to a suspension of **1** (1 g, 2.08 mmol) (m.p. 246 °C, prepared by a known procedure[3]) in 20 mL of acetone. The reaction mixture was stirred for 10 min at ~25 °C. The homogeneous reaction mixture was concentrated to 5 mL, diluted with 15 mL of a 2% aqueous solution of $NaHCO_3$, and extracted with AcOEt (3×60 mL). The extract was concentrated to dryness and the residue was chromatographed on a column with 40 g of SiO_2 (elution with $CHCl_3$—MeOH, 9 : 1) to give 1.05 g (97%) of compound **2**,

m.p. 223—224 °C, $[\alpha]_D^{18}$ +58.5 (*c* 0.9, $CHCl_3$) (*cf.* Ref. 6). The IR and ^1H NMR spectra were identical to those described previously.[5]

20-Hydroxyecdysone 2,3:20,22-diacetonide, or (20*R*,22*R*)-14α,25-dihydroxy-2β,3β:20,22-bis(isopropylidenedioxy)-5β-cholest-7-en-6-one (3). A suspension of **1** (1 g, 2.08 mmol) and phosphomolybdic acid (4 mg) in 25 mL of acetone was stirred for 35 min at ~25 °C. After homogenization (40 min), the reaction mixture was concentrated to 5 mL, diluted with 15 mL of a 2% solution of $NaHCO_3$, and extracted with AcOEt (3×60 mL). The extract was concentrated to dryness and the residue was chromatographed on a column with 50 g of SiO_2 (elution with $CHCl_3$—MeOH, 9 : 1) to give 0.95 g (82%) of compound **3**, m.p. 234—235 °C, $[\alpha]_D^{15}$ +39.4 (*c* 1.1, $CHCl_3$) (*cf.* Ref. 5). The IR and ^1H NMR spectra were identical to those described previously.[5]

20-Hydroxy-25-*O*-trifluoroacetylecdysone 20,22-acetonide, or 2β,3β,14α-trihydroxy-(20*R*,22*R*)-20,22-isopropylidenedioxy-25-trifluoroacetoxy-5β-cholest-7-en-6-one (4). Trifluoroacetic anhydride (0.16 g, 0.76 mmol) was added with stirring to a solution of compound **2** (0.2 g, 0.38 mmol) and 2 mL of Py in 3 mL of $CHCl_3$. The reaction mixture was stirred for 20 min at ~25 °C and concentrated, and the residue was chromatographed on a column with 25 g of SiO_2 (elution with $CHCl_3$—MeOH, 7 : 1) to give 0.18 g (77%) of compound **4**, m.p. 125—127 °C, $[\alpha]_D^{15}$ +33.1 (*c* 2.3, $CHCl_3$). Found (%): C, 62.18; H, 7.85. $C_{32}H_{47}F_3O_8$. Calculated (%): C, 62.34; H, 7.63. IR (KBr), ν/cm^{-1}: 1635, 1770, 3400. ^1H NMR ($CDCl_3$), δ: 0.76 (s, 3 H, H(18)); 0.93 (s, 3 H, H(19)); 1.14 (s, 3 H, H(21)); 1.32 and 1.41 (both s, 6 H, 20,22-Me_2C); 1.57 (s, 6 H, H(26), H(27)); 1.10—2.48 (m, 18 H, CH, CH_2); 3.04 (m, 1 H, H(9), $w_{1/2}$ = 26.0); 3.61 (m, 1 H, H(22)); 3.88—4.20 (m, 2 H, H(2), H(3)), 5.78 (m, 1 H, H(7), $w_{1/2}$ = 4.0).

20-Hydroxy-25-*O*-trifluoroacetylecdysone 2,3:20,22-diacetonide, or (20*R*,22*R*)-14α-hydroxy-2β,3β,20,22-bis(isopropylidenedioxy)-25-trifluoroacetoxy-5β-cholest-7-en-6-one (5). Trifluoroacetic anhydride (0.15 g, 0.7 mmol) was added with stirring to a solution of compound **3** (0.2 g, 0.35 mmol) and Py (2 mL) in 3 mL of $CHCl_3$. The reaction mixture was stirred for 10 min at ~25 °C (until the starting compound disappeared according to TLC on Silufol plates, elution with $CHCl_3$—MeOH, 10 : 1). The mixture was concentrated to dryness and the residue was chromatographed on a column with 40 g of SiO_2 (elution with $CHCl_3$—MeOH, 10 : 1) to give 0.18 g (78%) of compound **5**, m.p. 107—109 °C, $[\alpha]_D^{15}$ +3.2 (*c* 1.2, MeOH). Found (%): C, 64.39; H, 7.58. $C_{35}H_{51}F_3O_8$. Calculated (%): C, 64.01; H, 7.83. IR (KBr), ν/cm^{-1}: 1635, 1770, 3400. UV, λ_{max}/nm: 244. ^1H NMR ($CDCl_3$), δ: 0.76 (s, 3 H, H(18)); 0.95 (s, 3 H, H(19)); 1.12 (s, 3 H, H(21)); 1.29 (s, 6 H, 2,3-Me_2C); 1.38 and 1.40 (both s, 6 H, 20,22-Me_2C); 1.54 (s, 3 H, H(26)); 1.56 (s, 3 H, H(27)); 1.05—2.25 (m, 17 H, CH, CH_2); 2.29 (dd, 1 H, H(5), ^3J = 12.5 Hz, ^3J = 4.5 Hz); 2.81 (m, 1 H, H(9), $w_{1/2}$ = 24.0); 3.58 (dd, 1 H, H(22), ^3J = 9.6 Hz, ^3J = 2.2 Hz); 4.15—4.25 (m, 2 H, H(2), H(3)); 5.79 (d, 1 H, H(7), ^4J = 2.2 Hz).

14,15-Anhydro-20-hydroxy-25-*O*-trifluoroacetylecdysone 20,22-acetonide, or (20*R*,22*R*)-2β,3β-dihydroxy-20,22-isopropylidenedioxy-25-trifluoroacetoxy-5β-cholesta-7,14-dien-6-one (6). Trifluoroacetic anhydride (0.24 g, 1.14 mmol) was added with stirring to a solution of compound **2** (0.2 g, 0.38 mmol) and Py (2 mL) in 3 mL of $CHCl_3$. The reaction mixture was stirred for 12 min at ~25 °C (until the starting compound disappeared according to TLC on Silufol plates, elution with $CHCl_3$—MeOH, 10 : 1) and concentrated to dryness and the solid residue was chromatographed on a column with 20 g of SiO_2 (elution with $CHCl_3$—MeOH, 10 : 1) to give 0.19 g (83%) of compound **6**, m.p. 104—106 °C, $[\alpha]_D^{15}$ −150.3 (*c* 1.7, $CHCl_3$). Found (%): C, 64.54; H, 7.70. $C_{32}H_{45}F_3O_7$. Calculated (%): C, 64.20; H, 7.58. IR (KBr), ν/cm^{-1}: 1635, 1770, 3400. UV, λ_{max}/nm: 293. ^1H NMR ($CDCl_3$), δ: 0.82 (s, 3 H, H(18)); 0.88 (s, 3 H, H(19)); 1.03 (s, 3 H, H(21)); 1.15 and 1.27 (both s, 6 H, 20,22-Me_2C); 1.47 (s, 3 H, H(26)); 1.49 (s, 3 H, H(27)); 1.02—2.72 (m, 17 H, CH, CH_2); 3.57 (m, 1 H, H(22), $w_{1/2}$ = 15.0); 3.71 (m, 1 H, H(2), $w_{1/2}$ = 28.0); 3.96 (m, 1 H, H(3), $w_{1/2}$ = 11.0); 5.89 (m, 1 H, H(15), $w_{1/2}$ = 9.0); 6.01 (m, 1 H, H(7), $w_{1/2}$ = 6.0).

14,15-Anhydro-20-hydroxy-25-*O*-trifluoroacetylecdysone 2,3:20,22-diacetonide, or (20*R*,22*R*)-2β,3β:20,22-bis(isopropylidenedioxy)-25-trifluoroacetoxy-5β-cholesta-7,14-dien-6-one (7). Trifluoroacetic anhydride (0.22 g, 1.05 mmol) was added with stirring to a solution of compound **3** (0.2 g, 0.35 mmol) and Py (2 mL) in 3 mL of $CHCl_3$. The reaction mixture was stirred for 17 min at ~25 °C (until the starting compound disappeared according to TLC on Silufol plates, elution with $CHCl_3$—MeOH, 15 : 1) and concentrated to dryness, and the solid residue was chromatographed on a column with 40 g of SiO_2 (elution with $CHCl_3$—MeOH, 15 : 1) to give 0.19 g (85%) of compound **7**, m.p. 124—125 °C, $[\alpha]_D^{15}$ −203.6 (*c* 1.4, $CHCl_3$). Found (%): C, 65.98; H, 7.53. $C_{35}H_{49}F_3O_7$. Calculated (%): C, 65.81; H, 7.73. IR (KBr), ν/cm^{-1}: 1635, 1770, 3400. UV, λ_{max}/nm: 292. ^1H NMR ($CDCl_3$), δ: 0.76 (s, 3 H, H(18)); 0.95 (s, 3 H, H(19)); 1.12 (s, 3 H, H(21)); 1.29 (s, 6 H, 2,3-Me_2C); 1.38 and 1.46 (both s, 6 H, 20,22-Me_2C); 1.54 (s, 3 H, H(26)); 1.56 (s, 3 H, H(27)); 1.05—2.25 (m, 15 H, CH, CH_2); 2.29 (dd, 1 H, H(5), ^3J = 12.5 Hz, ^3J = 4.5 Hz); 2.81 (m, 1 H, H(9), $w_{1/2}$ = 24.0); 3.58 (dd, 1 H, H(22), ^3J = 9.6 Hz, ^3J = 2.2 Hz); 4.15—4.25 (m, 2 H, H(2), H(3)); 5.96 (m, 1 H, H(15), $w_{1/2}$ = 7.0); 6.06 (d, 1 H, H(7), ^4J = 2.2 Hz).

Stachisterone B 20,22-acetonide, or 14,15-anhydro-20-hydroxyecdysone 20,22-acetonide, or (20*R*,22*R*)-2β,3β,25-trihydroxy-20,22-isopropylidenedioxy-5β-cholesta-7,14-dien-6-one (8). A mixture of compound **6** (0.15 g, 0.25 mmol) in 5 mL of 80% aqueous MeOH and 0.02 g of $NaHCO_3$ was stirred for 36 h at ~25 °C and extracted with AcOEt (3×10 mL). The organic layers were combined, dried with $MgSO_4$, and concentrated. The solid residue was chromatographed on a column with 30 g of SiO_2 (elution with $CHCl_3$—MeOH, 10 : 1) to give 0.11 g (87%) of compound **8**, m.p. 124—125 °C, $[\alpha]_D^{17}$ −8.97 (*c* 0.7, MeOH). Found (%): C, 72.09; H, 9.31. $C_{30}H_{46}O_6$. Calculated (%): C, 71.68; H, 9.22. UV, λ_{max}/nm: 291. ^1H NMR ($CDCl_3$): 0.88 (s, 3 H, H(18)); 0.96 (s, 3 H, H(19)); 1.11 (s, 3 H, H(21)); 1.20 and 1.32 (both s, 6 H, 20,22-Me_2C); 1.47 and 1.49 (both s, 6 H, H(26), H(27)); 1.03—2.71 (m, 16 H, CH, CH_2), 3.20 (m, 1 H, H(9), $w_{1/2}$ = 28.0); 3.57 (dd, 1 H, H(22), ^3J = 9.8 Hz, ^3J = 2.0 Hz); 3.70 (m, 1 H, H(2), $w_{1/2}$ = 23); 3.96 (m, 1 H, H(3), $w_{1/2}$ = 11); 5.89 (m, 1 H, H(15), $w_{1/2}$ = 8); 6.01 (m, 1 H, H(7), $w_{1/2}$ = 4).

Stachisterone B 2,3:20,22-diacetonide, or 14,15-anhydro-20-hydroxyecdysone 2,3:20,22-diacetonide, or (20*R*,22*R*)-25-hydroxy-2β,3β:20,22-bis(isopropylidenedioxy)-5β-cholesta-7,14-dien-6-one (9). A similar procedure starting from 0.18 g (0.28 mmol) of compound **7** gave 0.13 g (85%) of compound **9**, m.p. 192—194 °C, $[\alpha]_D^{24}$ −128.6 (*c* 7.9, $CHCl_3$). Found (%): C, 72.81; H, 10.05. $C_{33}H_{50}O_6$. Calculated (%): C, 73.03; H, 9.29.

UV, λ_{max}/nm: 292. ^{1}H NMR ($CDCl_3$): 0.94 (s, 3 H, H(19)); 1.03 (s, 3 H, H(18)); 1.16 (s, 3 H, H(21)); 1.21 (s, 6 H, H(26), H(27)); 1.25 and 1.46 (both s, 6 H, 2,3-Me_2C); 1.27 and 1.37 (both s, 6 H, 20,22-Me_2C); 0.96—2.36 (m, 16 H, CH, CH_2); 2.62 (dd, 1 H, H(5), ^3J = 16.2 Hz, ^3J = 11.7 Hz); 3.70 (m, 1 H, H(22), $w_{1/2}$ = 14); 4.12 (ddd, 1 H, H(2), ^3J = 9.5 Hz, ^3J = 5.9 Hz, ^3J = 5.6 Hz); 4.22 (m, 1 H, H(3), $w_{1/2}$ = 10); 5.94 (t, 1 H, H(15), ^3J = 3.0 Hz); 6.06 (d, 1 H, H(7), ^3J = 2.0 Hz).

Stachisterone B, or 14,15-anhydro-20-hydroxyecdysone, or (20*R*,22*R*)-2β,3β,20,22,25-pentahydroxy-5β-cholesta-7,14-diene-6-one (10). ***A.*** A mixture of compound **8** (0.1 g, 0.2 mmol), 70% aqueous AcOH (1 mL), and $ZnCl_2$ (94 mg) was stirred for 4 h at ~25 °C. The reaction mixture was diluted with water (3 mL) and extracted with BuOH (3×10 mL). The organic layers were combined, washed with brine (30 mL) and dried with $MgSO_4$, and the solvent was evaporated. The solid residue was chromatographed on a column with 20 g of SiO_2 (elution with $CHCl_3$—MeOH, 5 : 1) to give 40 mg (43%) of compound **10**, m.p. 126—128 °C, $[\alpha]_D^{25}$ −87.8 (*c* 0.52, MeOH). Found (%): C, 70.15; H, 9.21. $C_{27}H_{42}O_6$. Calculated (%): C, 70.10; H, 9.15. The IR, UV, and ^{1}H NMR spectra (in C_5D_5N) were identical to those reported previously.[1,6] ^{1}H NMR (CD_3OD): 0.97 (s, 3 H, H(19)); 1.13 (s, 3 H, H(18)); 1.17 and 1.18 (both s, 6 H, H(26), H(27)); 1.27 (s, 3 H, H(21)); 0.83—2.41 (m, 15 H, CH, CH_2); 2.54—2.75 (m, 2 H, H(5), H(9)); 3.31 (m, 1 H, H(22)); 3.79 (m, 1 H, H(2), $w_{1/2}$ = 18); 3.92 (m, 1 H, H(3), $w_{1/2}$ = 9); 6.06 (m, 2 H, H(7), H(15), $w_{1/2}$ = 8).

B. A mixture of compound **9** (0.1 g, 0.18 mmol) and 70% aqueous AcOH (1 mL) was stirred for 1.5 h at ~20 °C, $ZnCl_2$ (84 mg) was added, and stirring was continued for 5 h. The reaction mixture was diluted with water (3 mL) and extracted with BuOH (3×10 mL). The organic layers were combined, washed with brine (30 mL), dried with $MgSO_4$, and concentrated. The solid residue was chromatographed on a column with 20 g of SiO_2 (elution with $CHCl_3$—MeOH, 5 : 1) to give 35 mg (42%) of compound **10** identical to the product prepared by method ***A*** (^{1}H and ^{13}C NMR spectra).

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