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Ozonolysis of Alkenes and Study of Reactions of Polyfunctional Compounds: LXVI.* Ozonolysis and Hydrogenation of Diacetonides of 24,25- and 25,26-Anhydro-20-hydroxyecdysones. Synthesis of Ponasterone A**

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Abstract—Ozonolysis of 2,3:20,22-diacetonides of 24.25-and 25,26-anhydro-20-hydroxyecdysones afforded the corresponding ω-carbonyl derivatives. The hydrogenation of the mentioned dehydration products of 20-hydroxyecdysone acetonide yielded diacetonide of ponasterone A that provided ponasterone A and its 29,22-acetonide at hydrolysis.

Ecdysteroids function as hormones of shedding, metamorphosis, and diapause in insects and crustaceans. They are also found in considerable concentrations in many kinds of plants. Therefore the substances are promising for practical application in medicine and agriculture [2].

20-Hydroxyecdysone, the main component of the ecdysteroid composition of a number of plant species, is among the most accessible phitoecdysteroids [3]. Chemical transformations of this phitoecdysteroid open up new vistas for synthesis of other less accessible ecdysteroids, in particular, proceeding from products of its dehydration at 25-hydroxy group abutasterone, pterosterone and their 24-epimers were prepared [4, 5].

We carried out ozonolysis of a mixture that formed at treating 2,3:20,22-diacetonide of 20-hydroxyecdysone (**I**) with mesyl chloride in the presence of pyridine and *N*,*N*-diaminopyridine. The mixture according to ^{1}H NMR spectrum contained in ~3 : 1 ratio 24,25-(**II**) and 25,26-anhydro-20-hydroxyecdysones **III**. The ozonolysis afforded the corresponding ω-carbonyl-containing compounds that would be used in the syntheses of some ecdysteroids and their analogs. On the other hand, the hydrogenation of olefins **II** and **III** opened a simple route to the synthesis of ponasterone A that was a hormone of crustaceans and was also detected in plants [2, 6].

It was established that ozonolysis of a mixture of olefins **II** and **III** in dichloromethane followed by hydrogenation of the peroxy products on Lindlar catalyst afforded aldehyde **IV**, its hemiacetal **V**, and ketone **VI**. The column chromatography on SiO_2 provided a mixture of aldehyde **IV** with its hemiacetal **V** (in ~1 : 3 ratio as showed the intensity ratio of CHO and OCH_3 signals in the ^{1}H NMR spectrum), and ketone **VI**. The presence in the ^{13}C NMR spectrum of compounds **IV**–**VI** a single resonance of quaternary carbon at δ_C 107 ppm corresponding to the group 20.22-Pr-*i* (see the table) evidences that the 2,3-acetonide protection was removed obviously by hydrogenolysis during the reduction of peroxides. Actually, the diacetonide was conserved when the ozonation of the mixture of olefins **II** and **III** was performed in acetone in the presence of $Ba(OH)_2$ when the peroxides reduction was not required because their decomposition during the ozonolysis was effected by the base [7]. Under conditions of this "nonperoxide" ozonolysis arose a mixture of aldehyde **VII** and ketone **VIII** that was separated by column chromatography. Ketone **VIII** was identical to the compound we prepared from monoacetonide **VI** by treating it with acetone under standard conditions [8]. In the ^{13}C NMR spectra of compounds **VII** and **VIII** characteristic signals are observed at δ 200.3 (CHO) and 208.5 (CO) respectively (see the Scheme).

Hydrogenation of the mixture of olefins **II** and **III** on Raney nickel afforded diacetonide of ponasterone **IX** that by hydrolysis with 70% AcOH was converted

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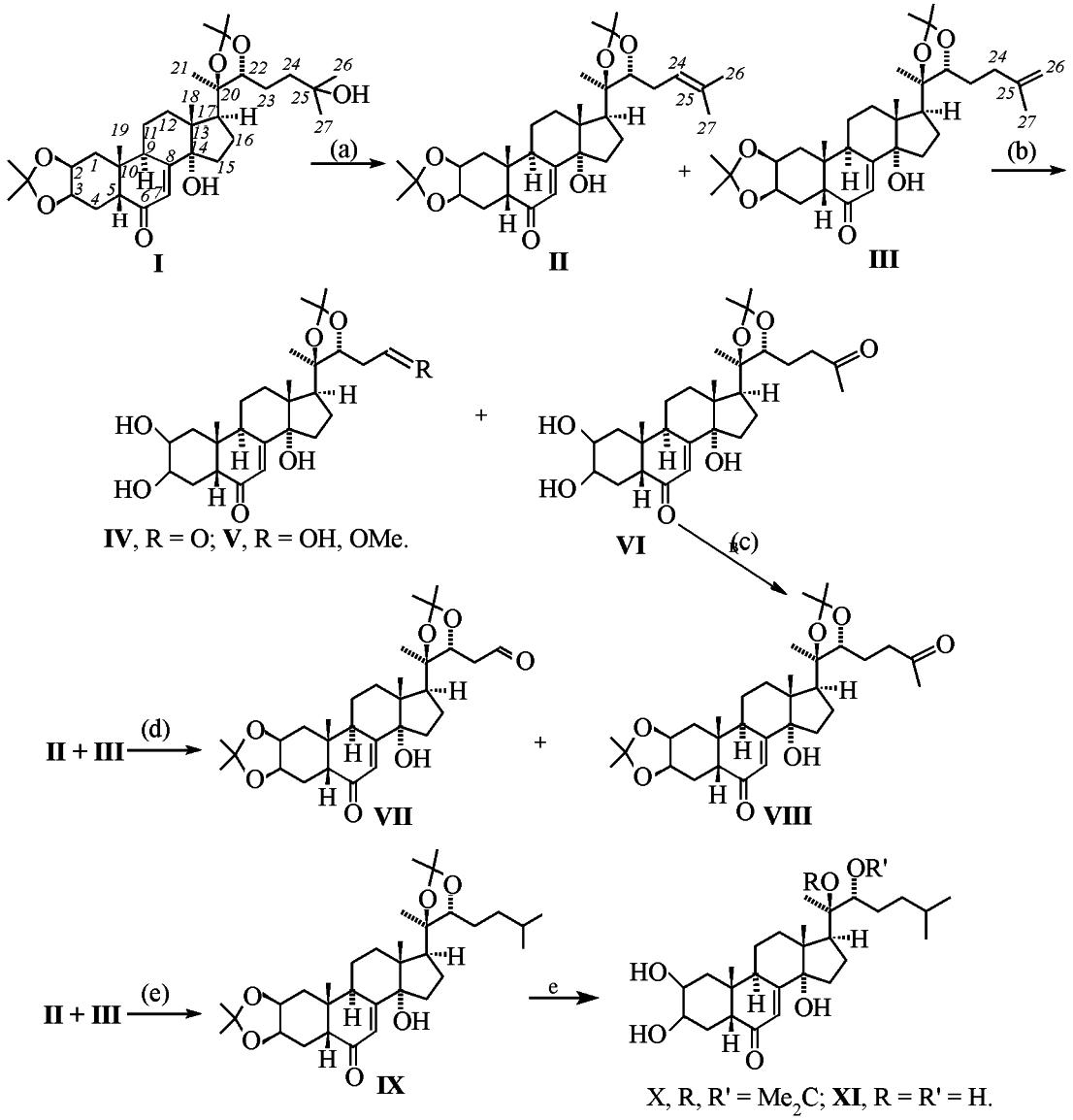

23.04.2002(**a**) MsCl/Py/$Me_2NC_5H_4N$; (**b**) O_3/CH_2Cl_2–MeOH, H_2/Pd-$CaCO_3$-PbO; (**c**) Me_2CO/h^+; (**d**) $O_3/Ba(OH)_2$, Me_2CO; (**e**) H_2/Ni–Ra; (**f**) AcOH, $ZnCl_2$.

into monoacetonide **X** as evidenced the ^{13}C NMR spectrum of the latter compound containing a signal at δ 106.7 ppm corresponding to the acetal atom of the group 20,22-Pr-*i*. Both acetonide groups were removed from compound **IX** by AcOH with $ZnCl_2$ along procedure [9]. The treatment furnished a mixture of monoacetonide **X** and ponasterone **XI** that was isolated by column chromatography. In the ^1H NMR of each compound are present two characteristic doublets in the O.8–0.9 ppm region (*J* 6.5 Hz) belonging to protons of geminal methyl groups attached to the tertiary carbon C^{25}. In the ^{13}C NMR spectrum of compounds **IX**–**XI** the signals from C^{25} atom appear at δ 28–29 ppm and thus are considerably shifted upfield (Δδ ~43 ppm) with respect to the signal of the C^{25} atom of initial compound **I**.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord 75IR from KBr pellets. ^1H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-300 at operating frequencies 300.13 and 75.25 MHz respectively, solvent $CDCl_3$ or C_5D_5N, internal reference TMS. Melting points were determined on Boëtius heating block. The optical rotation was measured on polarimeter Perkin-Elmer-141. TLC was performed on Silufol plates with SiO_2,

^{13}C NMR spectra (δ, ppm) of compounds **I**–**XI**

Atom no.	**I**	**IIa**	**IIIa**	**IVa**	**Va**	**VI**	**VII**	**VIII**	**IX**	**X**	**XI**
	$CDCl_3$	$CDCl_3$	$CDCl_3$	C_5D_5N	C_5D_5N	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	CD_3OD
1	37.5	37.6	37.6	37.1	37.1	36.4	37.5	37.6	37.4	36.6	37.5
2	72.0	72.1	72.1	67.4	67.4	67.6	72.1	72.1	72.0	67.7	68.8
3	71.5	71.6	71.6	67.3	67.3	67.4	71.5	71.6	71.5	67.4	68.6
4	31.3	31.6	31.6	31.8	31.8	31.3	31.7	31.5	31.4	31.5	32.9
5	50.7	50.8	50.8	50.6	50.6	50.1	50.8	50.8	50.7	50.0	51.8
6	203.0	202.8	202.8	203.5	203.5	204.7	202.9	202.8	202.9	204.6	206.5
7	121.1	121.2	121.2	121.1	121.1	121.3	121.4	121.2	121.1	121.4	122.2
8	163.8	163.4	163.4	165.4	165.4	165.7	163.0	163.3	163.8	165.6	168.0
9	34.4	34.6	34.6	33.8	33.8	33.7	34.3	34.5	34.3	36.5	35.2
10	37.7	37.7	37.7	38.5	38.5	38.2	37.8	37.7	37.6	38.2	39.3
11	20.4	20.5	20.5	20.3	20.3	20.4	20.4	20.5	20.4	20.4	21.6
12	30.8	31.0	31.0	31.0	31.0	30.9	30.9	30.9	30.8	31.0	32.6
13	47.4	47.5	47.5	47.2	47.2	47.2	47.4	47.4	47.3	47.3	[b]
14	84.6	84.9	84.9	84.2	84.2	84.6	84.8	84.7	84.6	84.7	85.3
15	26.5	26.9	29.6	29.3	29.3	28.9	26.6	26.8	30.8	29.6	31.8
16	21.1	21.1	21.1	21.3	21.3	21.1	21.1	21.1	21.1	21.3	21.6
17	48.9	49.1[c]	49.2[c]	48.9	48.9	48.9	48.8	48.8	48.9	49.1	50.5
18	16.9	17.0[c]	17.1[c]	16.7[c]	16.6[c]	17.0	17.0	16.9	16.9	16.2	18.1
19	23.5	23.6	23.6	23.7	23.7	23.9	23.6	23.5	23.5	23.8	24.4
20	84.3	84.1	84.1	83.6	83.6	84.2	83.9	83.7	84.0	84.2	77.9
21	21.8	21.8	21.8	21.9	21.9	21.7	22.1	21.8	21.8	21.9	21.0
22	81.9	81.0c	80.7[c]	75.5	75.5	80.4	75.3	80.4	81.6	81.7	78.0
23	23.5	26.7	27.8	42.3	30.8	22.9	43.2	22.5	26.7	26.8	30.5
24	41.3	120.3	35.1	200.4	107.2	41.1	200.3	41.0	36.3	36.5	37.7
25	70.3	133.5	145.3	–	–	209.0	–	208.5	28.2	29.0	29.3
26	28.9	25.6	110.0	–	–	30.1	–	28.9	22.5	22.6	23.4
27	28.4	18.0	22.5	–	–	–	–	–	22.4	22.5	22.8
2,3-	108.2	108.2	108.2	–	–	–	108.3	108.3	108.1	–	–
i-PrO_2	26.4	26.4	26.4	–	–	–	26.4	27.0	26.3	–	–
	29.2	28.5	28.5	–	–	–	28.5	28.5	28.4	–	–
20,22-	106.9	106.8	106.8	107.3	107.3	107.0	108.0	106.9	106.6	106.7	–
i-PrO_2	26.8	26.8	26.8	26.5	26.5	26.9	26.9	26.6	26.5	27.8	–
	29.5	28.9	28.9	28.5	28.5	28.9	31.0	29.0	28.9	28.3	–

[a] Assignment of signals was done for mixtures **II** and **III**, **IV** and **V**.

[b] Superimposed on the multiplet of solvent (δ 49 ppm).

[c] The position of signals may be interchanged.

development with a solution of vanillin in ethanol acidified with sulfuric acid. ^{13}C NMR spectra of compounds **I**–**XI** are given in the table.

2,3:20,22-Diacetonide of stachysterone C, or (20*R*,22*R*)-14α-hydroxy-2β,3β:20,22-bis-O-isopropylidene-5β-cholesta-7,24-dien-6-one (II), and 2,3:20,22-diacetonide of 25,26-didehydroponasterone A, or (20*R*, 22*R*)-14α-hydroxy-2β,3β:20,22-bis-O-isopropylidene-5β-cholesta-7,25-dien-6-one (III). To a solution of 1.55 g (2.78 mmol) of diacetonide **I** (prepared by procedure [8] from 20-hydroxyecdysone isolated from a plant *Serratula coronata* [10]) in anhydrous pyridine (5 ml) was added while stirring at 0–5°C 1 ml (12.78 mmol) of mesyl chloride and then 0.05 g (15 mol%) of *N*,*N*-dimethylaminopyridine. The reaction mixture was stirred for 20 min at 5°C and 4 h at room temperature. Then 5 ml of water was added, and the reaction products were extracted into chloroform (3×35 ml). The extract

was washed with water, dried with Na_2SO_4, and evaporated in a vacuum. The residue was subjected to column chromatography on silica gel (eluent $CHCl_3$–MeOH, 99 : 1). We obtained 1.32 g (87%) of a mixture of alkenes **II** and **III** (in the 3 : 1 ratio according to ^{1}H NMR data). IR and NMR spectra were consistent with previously published [4].

20,22-Acetonide of 24-oxo-25,26,27-trisnorponasterone A, or (20*R*,22*R*)-2β,3β,14α-trihydroxy-20,22-*O*-isopropylidene-24-oxo-25,26,27-trisnor-5β-cholest-7-en-6-one (IV), 20,22-acetonide of 24-hydroxy-24-methoxy-25,26,27-trisnorponasterone A, or (20*R*,22*R*)-2β,3β,14α,24-tetrahydroxy-20,22-*O*-isopropylidene-24-methoxy-25,26,27-trisnor-5β-cholest-7-en-6-one (V), and 20,22-acetonide of 25-oxo-27-norponasterone A, or (20*R*,22*R*)-2β,3β,14α-trihydroxy-20,22-*O*-isopropylidene-25-oxo-27-nor-5β-cholest-7-en-6-one (VI). Through a solution of 0.15 g (0.28 mmol) of a mixture of alkenes **II** and **III** in 12.9 ml of CH_2Cl_2–MeOH (2 : 1) at –70°C was bubbled an ozone-oxygen mixture at a rate 70 ml min^{-1} for 180 s (till 0.28 mmol of O_3 was consumed). The reaction mixture was flushed with argon, 2 mg of Lindlar catalyst was added, and the mixture was stirred under hydrogen atmosphere till all the peroxides were reduced (test with iodo-starch indicator). The catalyst was then filtered off, the filtrate was evaporated, and the residue was subjected to chromatography on a column charged with 5 g of SiO_2 (eluent $CHCl_3$–MeOH, 20 : 1). We isolated 0.04 g of a mixture of aldehyde **IV** (R_f 0.27) and hemiacetal **V** (R_f 0.27), and 0.05 g of ketone **VI** (R_f 0.45).

Mixture of aldehyde IV and hemiacetal V. IR spectrum (KBr), ν, cm^{-1}: 1680 s 1715 v.s, 3450, ($w_{h/2}$ 180). ^{1}H NMR spectrum (C_5D_5N), δ, ppm, *J*, Hz: 1.01 s (3H, H_3C^{18}), 1.05 s (3H, H_3C^{21}), 1.32 s (3H, H_3C^{19}), 1.15–2.85 m (15H, CH, CH_2), 1.48 s and 1.56 s (6H, $2CH_3$ from *i*-PrO_2-20,22), 2.97 d.d (1H, HC^5, ^3J 5.0 and 12.0), 3.61 m (1H, HC^9, $w_{1/2}$ 26.0 Hz), 4.09 s (2.25 H, OCH_3), 4.12 (1H, HC^2, $w_{1/2}$ 20.0 Hz), 4.31 m (1H, HC^3, $w_{1/2}$ *18.0 Hz), 4.38 m (1H, HC*^{22}, $w_{1/2}$ 25.0 Hz), 4.56 m (0.75H, OCHO, $w_{1/2}$ 20.0 Hz), 6.27 d (1H, HC^7, ^4J 2.0), 9.98 t (0.25H, CHO, ^3J 2.0).

Ketone VI. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J*, Hz: 0.77 s (3H, H_3C^{18}), 0.95 s (3H, H_3C^{19}), 1.14 s (3H, H_3C^{21}), 1.39 s and 1.40 s (6H, 2 CH_3 from *i*-PrO_2-20,22), 1.21–2.81 m (16H, CH_2), 2.16 s (3H, H_3C^{26}), 2.50 m (3H, HC^5, HC^9, HC^{17}), 3.58–3.86 m (2H, HC^2, HC^3), 4.56 m (1H, HC^{22}, $w_{1/2}$ 25.0 Hz), 5.82 d (1H, HC^7, ^4J 2.0). Found, %: C 68.98; H 8.81. $C_{29}H_{44}O_7$. Calculated, %: C 69.02; H 8.79.

2,3:20,22-Diacetonide of 24-oxo-25,26,27-trisnorponasterone A, or (20*R*,22*R*)-14α-hydroxy-2β,3β:20,22-bis-*O*-isopropylidene-24-oxo-25,26,27-trisnor-5β-cholest-7-en-6-one (VII), and 2,3:20,22-diacetonide of 25-oxo-27-norponasterone A, or (20*R*, 22*R*)-14α-hydroxy-2β3,β:20,22-bis-O-isopropylidene-25-oxo-27-nor-5β-cholest-7-en-6-one (VIII). Through a mixture of 0.2 g (0.37 mmol) of alkenes **II** and **III**, 0.13 g (0.41 mmol) of $Ba(OH)_2$, 0.5 ml of H_2O, and 3 ml of acetone at room temperature while vigorous stirring was passed a flow of ozone-oxygen mixture at a rate of 70 ml min^{-1} for 240 s (till 0.37 mmol of ozone was consumed). After completion of the reaction the precipitate was filtered off, the filtrate was evaporated in a vacuum, and the residue was subjected to chromatography on a column charged with 8 g of SiO_2 (eluent $CHCl_3$–MeOH, 19 : 1). We isolated 0.03 g of aldehyde **VII** (R_f 0.13) and 0.04 g of ketone **VIII** (R_f 0.37).

Aldehyde (VII). mp 129–131°C, $[\alpha]_D^{22}$ +56.9° (*c* 2.5, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1650 s, 1720 v.s, 2720 w, 3450 ($w_{h/2}$ 180). ^{1}H NMR ($CDCl_3$), δ, ppm, *J*, Hz: 0.79 s (3H, H_3C^{18}), 0.98 s (3H, H_3C^{19}), 1.18 s (3H, H_3C^{21}), 1.23 s, 1.33 s, 1.37 s and 1.43 s [12H, $4CH_3$ from 2(*i*-PrO_2)], 1.15–2.73 m (16H, CH, CH_2), 2.82 m (1H, HC^9, $w_{1/2}$ 24.0 Hz), 4.18–4.31 m (3H, HC^2, HC^3, HC^{22}), 5.81 d (1H, HC^7, ^4J 2.0), 9.83 br.s (1H, CHO, $w_{1/2}$ 6.0 Hz). Found, %: C 69.62; H 8.73. $C_{30}H_{44}O_7$. Calculated, %: C 69.74; H 8.58.

Ketone (VIII). mp 113–115°C, $[\alpha]_D^{22}$ +46.40 (*c* 1.7, $CHCl_3$), IR spectrum (KBr), ν, cm^{-1}: 1660 s, 1720 v.s., 3450 ($w_{h/2}$ 180). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J*, Hz: 0.77 s (3H, H_3C^{18}), 0.96 s (3H, H_3C^{19}), 1.13 s (3H, H_3C^{21}), 1.29 s, 1.31 s, 1.37 s and 1.39 s [12H, $4CH_3$ from 2(*i*-PrO_2)], 1.12–2.76 m (18H, CH, CH_2), 2.13 s (3H, H_3C^{26}), 2.81 m (1H, HC^9, $w_{1/2}$ 25.0 Hz), 4.15– 4.36 m (3H, HC^2, HC^3, HC^{22}), 5.79 d (1H, HC^7, ^4J 2.0). Found, %: C 70.28; H 8.95. $C_{32}H_{48}O_7$. Calculated, %: C 70.56; H 8.88.

Diacetonide of ketone VIII. To a solution of 0.05 g (0.1 mmol) of monoacetonide **VI** in 12 ml of anhydrous acetone was added 1.4 mg of phosphomolybdic acid. The mixture was stirred for 24 h at room temperature, and then it was boiler till complete conversion of the initial compound **VI** (3 h, TLC monitoring). The reaction mixture was evaporated, diluted with water, the reaction product was extracted into

chloroform (3 ×20 ml), The combined organic solutions were washed in succession with saturated solutions of $NaHCO_3$ and NaCl, dried with $MgSO_4$, and evaporated. The residue was subjected to chromatography on a column charged with 3 g of SiO_2 (eluent $CHCl_3$–MeOH, 10 : 1). We isolated 0.053 g (98%) of diacetonide **VIII** identical to the above described.

2,3:20,22-Diacetonide of ponasterone A, or (20*R*,22*R*)-14α-hydroxy-2β,3β:20,22-bis-*O*-isopropylidene-5β-cholest-7-en-6-one (IX). Through a dispersion of 0.1 g of the mixture of alkenes **II** and **III**, 0.05 g of Raney nickel, and 5 ml of ethanol was passed hydrogen at room temperature for ~16 h (TLC monitoring). On completion of reaction the catalyst was filtered off, the filtrate was evaporated, and the residue was subjected to chromatography on a column charged with 6 g of SiO_2 (eluent $CHCl_3$–MeOH, 20 : 1). We isolated 0.01 g (98%) of compound **IX**, R_f 0.51, mp 100–102°C, $[\alpha]_D^{19}$ +31.8° (*c* 3.07, $CHCl_3$). IR spectrum (KBr), ν, cm^{-1}: 1660, 3500. ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J*, Hz: 0.75 s (3H, H_3C^{18}), 0.86 d (6H, H_3C^{26}, H_3C^{27}, ^3J 6.5), 0.94 s (3H, H_3C^{19}), 1.10 s (3H, H_3C^{21}), 1.29 s, 1.37 s and 1.45 s [2:1:1, 12H, $4CH_3$ from 2(*i*-PrO_2)], 1.10–2.32 m (19H, CH, CH_2), 2.79 m (1H, HC^9, $w_{1/2}$ 25.0 Hz), 3.58 m (1H, HC^{22}, $w_{1/2}$ 13.0 Hz), 4.13–4.27 m (2H, HC^2, HC^3), 5.77 d (1H, HC^7, ^4J 2.0). Found, %: C 72.79; H 9.71. $C_{33}H_{52}O_6$. Calculated, %: C 72.75; H 9.62.

20,22-Acetonide of ponasterone A, or (20*R*,22*R*)-2β,3β14α-trihydroxy-20,22-*O*-isopropylidene-5β-cholest-7-en-6-one (X). A mixture of 100 mg (0.18 mmol) of diacetonide **IX** and 1 ml of 70% acetic acid was stirred at room temperature till complete conversion of the substrate (1.5 h, TLC monitoring). The reaction mixture was diluted with 3 ml of water and extracted with butanol (3 × 10 ml). The combined organic solutions were washed with saturated solution of NaCl, evaporated in a vacuum, and the residue was subjected to chromatography on a column charged with 4 g of SiO_2 (eluent $CHCl_3$–MeOH, 10 : 1). We isolated 0.091 g (98%) of compound **X**, mp 142–145°C, $[\alpha]_D^{22}$ +22.7° (*c* 2.48, $CHCl_3$). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J*, Hz: 0.78 s (3H, H_3C^{18}), 0.89 d (6H, H_3C^{26}, H_3C^{27}, ^3J 6.4), 0.96 s (3H, H_3C^{19}), 1.14 s (3H, H_3C^{21}), 1.32 s and 1.40 s (6H, $2CH_3$ from *i*-PrO_2), 1.10–2.43 m (19H, CH, CH_2), 3.07 m (1H, HC^9, $w_{1/2}$ 26.0 Hz), 3.62 m (1H, HC^{22}, $w_{1/2}$ 16.0 Hz), 3.89 m (1H, HC^2, $w_{1/2}$ 25.0 Hz), 3.98 m (1H, HC^3, $w_{1/2}$ 17.0 Hz), 5.82 d (1H, HC^7, ^4J 2.0). Found, %: C 71.37; H 9.62. $C_{30}H_{48}O_6$. Calculated, %: C 71.39; H 9.59.

Ponasterone A, or (20*R*,22*R*)-2β,3β14α,20,22-pentahydroxy-5β-cholest-7-en-6-one (XI). A mixture of 100 mg (0.18 mmol) of diacetonide **IX** and 1 ml of 70% acetic acid was stirred at room temperature for 1.5 h. Then 85 mg of zinc chloride was added, and the stirring continued for 5 h. The reaction mixture was diluted with 3 ml of water and extracted with butanol (3 × 10 ml). The combined organic solutions were washed with saturated solution of NaCl, dried with $MgSO_4$, evaporated in a vacuum, and the residue was subjected to chromatography on a column charged SiO_2 (eluent $CHCl_3$–MeOH, 30 : 1). We obtained 40 mg (43%) of compound **X** (R_f 0.32), identical to that described above, and 20 mg (24%) of compound **XI** (R_f 0.26), mp 255–258°C {259–260°C (decomp.) [6]}, $[\alpha]_D^{20}$ +59.2° (*c* 0.95, MeOH). ^1H NMR spectrum (CD_3OD), δ, ppm, *J*, Hz: 0.88 s (3H, H_3C^{18}), 0.90 d and 0.91 d (6H, H_3C^{26}, H_3C^{27}, ^3J 6.4), 0.96 s (3H, H_3C^{19}), 1.17 s (3H, H_3C^{21}), 1.10–2.42 m (19H, CH, CH_2), 3.14 m (1H, HC^9, $w_{1/2}$ 27.0 Hz), 3.36 m (1H, HC^{22}), 3.83 d.t (1H, HC^2, ^3J 12.0 and 4.0), 3.93 m (1H, HC^3, $w_{1/2}$ 14.0 Hz), 5.79 d (1H, HC^7, ^4J 2.0).

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