ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 11, pp. 1614–1618. © Pleiades Publishing, Ltd., 2008.
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Synthesis of 22- and 23-Oxoderivatives of 28-Homocastasterone

R. P. Litvinovskaya, M. E. Raiman, and V. A. Khripach

Institute of Bioorganic Chemistry, National Academy of Sciences of Belarus, Minsk, 220141Belarus
e-mail: litvin@iboch.bas-net.by

Received January 14, 2008

Abstract—A synthesis was performed of 22- and 23-oxoderivatives of 28-homocastasterone from 28-homosecasterine converted into a 22,23-diacetoxy derivative whose selective deacetyulation and successive oxidation of the formed 23-acetoxy-22-hydroxysteroid by Dess–Martin procedure led to the formation of 22-oxoderivative. *cis*-Hydroxylation of the Δ^2-bond in the latter by osmium tetraoxide and the hydrolysis of the acetate group made it possible to obtain 22-oxo-28-homocastasterone. Similarly 23-oxo-28-homocastasteron was synthesized from 22-acetoxy-23-hydroxy derivative obtained from the 23-acetoxy-22-hydroxysteroid by boiling in acetic acid in the presence of boron trifluoride etherate.

DOI: 10.1134/S1070428008110080

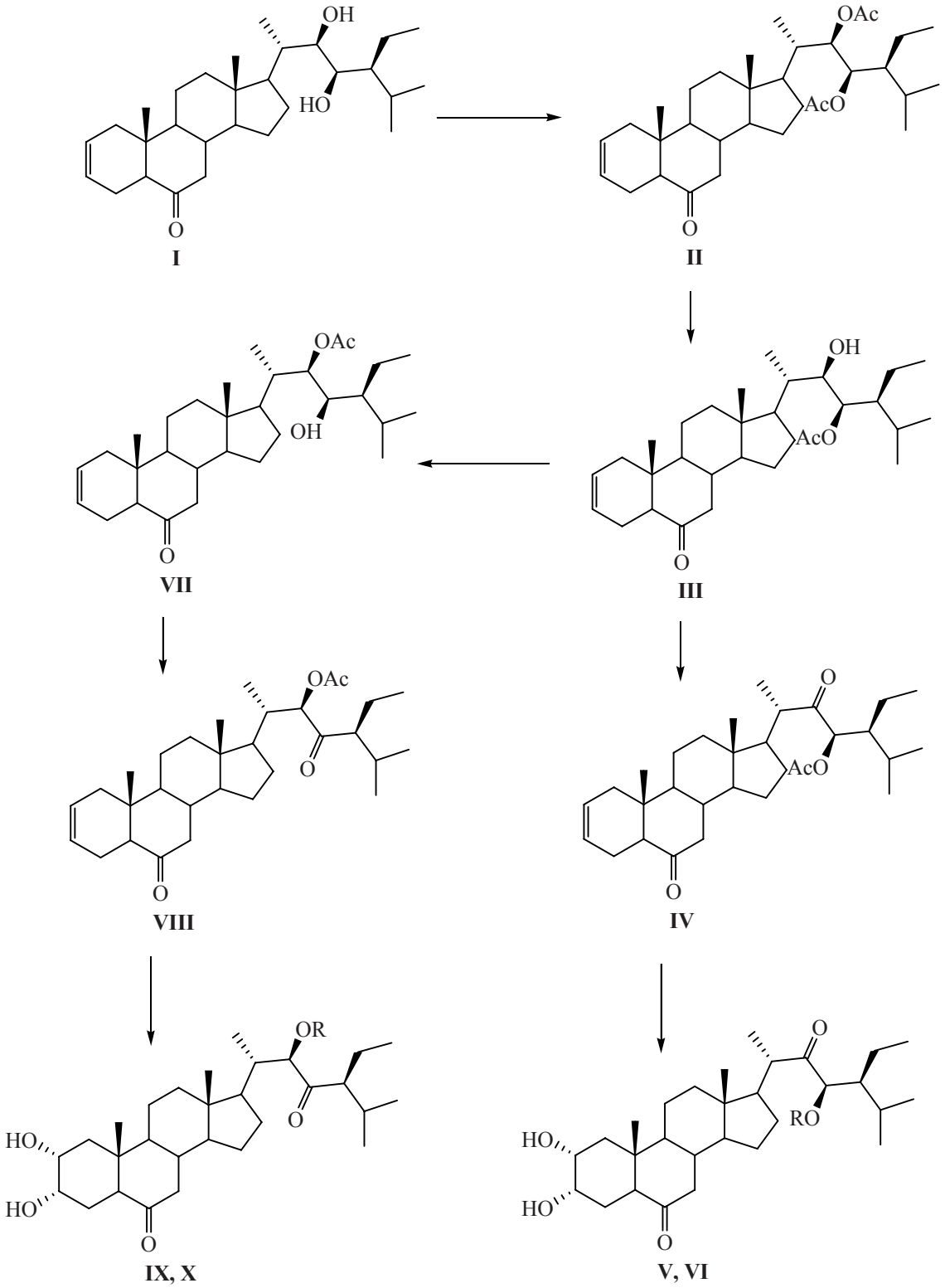
From the traditional viewpoint the biological activity of brassinosteroids is governed by the presence of 2α,3α- and 22*R*,23*R*-diol moieties in the side chain and also of 6-oxo- or 6-oxo-7-oxa groups in the cyclic part of the molecule at a *trans*-junction of the A,B cycles [1, 2]. The study of biological activity of brassinosteroids and their synthetic analogs often gives unexpected results. The activity comparable with that of the most studied brassinosteroids (24-epibrassinolide and 28-homobrassinolide) was found, for instance, in derivatives based on androstane [3], 6-deoxo- [4] and 22*R*,23*R*-epoxybrassinosteroids [5], brassinosteroid analogs with heterocycles in the side chain [6] etc. The research is actively carried out on isolation and identification of new brassinosteroid structure from various plants. In this connection goes on the development of synthetic schemes for naturally occurring brassinosteroids, the search for new active analogs, development of the methods for their detection and establishment of their structure. The target of this study is the synthesis of analogs of 28-homobrassinosteroids with an oxo group in the side chain. These compounds may be promising by their biological activity and convenient intermediates for various modifications.

This paper reports on the development of synthetic schemes for 22- and 23-oxo analogs of 28-homocastasterone. We chose as the initial compound 28-homosecasterine (**I**) synthesized in 8 stages from stigmasterine [7]. The attempt of selective acylation of 22,23-diol **I** with acetic anhydride in pyridine was not successful since the 22- and 23-hydroxy groups were acetylated virtually simultaneously giving a mixture of 22- and 23-monoacetoxy derivatives that further converted into 22,23-diacetoxy-28-homosecasterine (**II**) (see the scheme).

The first stage of the scheme we developed was a selective deacetylation of 28-homosecasterine 22,23-diacetate **II** by treating with 5% solution of K_2CO_3 in methanol at room temperature. The partial deacetylation monitored by TLC occurred with primary removal of the 22-acetoxy group. After 2–2.5 h remained only 22-monohydroxy derivative that further converted into 22,23-diol **I**, therewith for 4–5 h the reaction mixture contained the initial diacetate **II**. Terminating the reaction after 2–2.5 h we isolated up to 40% of monoacetate **III** at 53% recovery of initial compound **II**. 23-Acetoxy-22-hydroxy derivative **III** contained in the ^{1}H NMR spectrum a single tree-proton singlet of the acetate methyl group at δ 2.09 ppm and a one-proton triplet at δ 3.72 ppm belonging to the proton at C^{22}; the proton signal at C^{23} was unchanged. In the IR spectrum appeared the stretching vibrations bands of the ester moiety (ν 1735 and 1250 cm^{-1}), and the absorption band of the hydroxy group was simplified.

Monoacetate **III** was oxidized under mild conditions by Dess–Martin [8] to obtain 23-acetoxy-22-oxo-28-

Scheme.



R = Ac (**V, IX**), H (**VI, X**).

homosecasterine (**IV**) that was confirmed by the appearance in the IR spectrum of the second band of the stretching vibrations of a keto group (ν 1720 cm^{-1}) and the lack of the hydroxy group absorption. In the ^{13}C NMR spectrum appeared an additional signal of carbonyl carbon of the acetate group (δ 172.7 ppm), and in the ^{1}H NMR spectrum the signal of proton on the carbon atom linked to hydroxy group disappeared.

The scheme was completed by the *cis*-hydroxylation of the Δ^2-bond in compound **IV** with potassium osmate dihydrate in the presence of 10,11-dihydroquinidine *p*-chlorobenzoate [9] to obtain 2α,3α-diol **V**. The structure of compound **V** is confirmed by the presence in the IR spectrum of a strong absorption band in the region of the stretching vibrations of hydroxy groups, and also by the disappearance from the ^{1}H NMR spectrum of the signals of olefin protons and the presence of two signals of methine protons H^{2} and H^{3} at the carbon atoms linked to the hydroxy groups (δ 3.75 and 4.05 ppm). The subsequent removal of the acetate protection by treating with a methanol solution of potassium carbonate led to the formation of the target 22-oxo-28-homocastasterone (**VI**).

The key stage in the preparation of 23-oxoderivatives became the transacylation of 23-acetoxy-22-hydroxy derivative **III** that we discovered. The boiling of compound **III** in acetic acid in the presence of boron trifluoride etherate resulted in the formation in 48% yield of 22-acetoxy-23-hydroxy derivative **VII**. Among the parameters distinguishing monoacetates **III** and **VII** in the ^{1}H NMR spectra the most prominent are the form and position of proton signals at C^{22} and C^{23}. In the spectrum of obtained 22-acetoxy derivative **VII** the signal of the proton attached to the carbon atom bearing a hydroxy group is observed as a multiplet in a weaker field (δ 3.83 ppm), and the methine proton at C^{22} appears upfield (δ 5.04 ppm) compared to the spectrum of the 23-acetoxy-22-hydroxy analog **III**.

The oxidation of hydroxy derivative **VII** under the condition used in the oxidation of compound **III** led to ketone **VIII**, regiomer of compound **IV**. In this case also the signal of the proton at the carbon linked to acetoxy group is observed upfield (δ 5.18 instead of 5.28 ppm) in the ^{1}H NMR spectrum, however the most characteristic is the proton signal of methyl group at C^{20}. Its downfield shift compared with regiomer **IV** is very large and amounts to 0.31 ppm. A similar pattern we had observed before. For instance, at the oxidation of 23-bromo-22-hydroxysteroids the signal of protons from the methyl group in the position *21* displaced by 0.16 ppm [10], and on the oxidation of 22,24-dihydroxy-24-methylsteroids this signal shifted by 0.15 ppm [11]. The characteristic for establishing the regioisomeris of acetoxyketones **IV** and **VIII** and also of their derivatives became the multiplet signal from the methine proton at C^{20} whose downfield position (δ 2.64 ppm) corresponded to 22-oxoderivative whereas the analogous signal for the 23-oxosteroid appeared more upfield (δ 2.33–2.39 ppm) [9].

The diol moiety into the position 2α,3α was introduced, like with compound **IV**, by *cis*-hydroxylation of the Δ^2-bond in olefin **VIII**. The removal of the acetate group in obtained compound **IX** gave 2,3,22-triol **X**, 23-oxo-analog of 28-homocastasterone.

The obtained 2,3-dihydroxy- (**IX**) and 2,3,22-trihydroxy derivative (**X**), regiomers of compounds **V** and **VI**, have spectral relations characteristic of their Δ^2-analogs.

EXPERIMENTAL

^{1}H and ^{13}C NMR were registered on a spectrometer Bruker A-500 (operating frequency 500 MHz) from solutions in deuterochloroform applying TMS for internal reference. IR spectra were recorded on a spectrophotometer UR-20. Mass spectra were measured on an instrument Hewlett Packard-5890 in an electron impact mode (EI) at the energy of ionizing electrons 70eV, or on an instrument AMD 402 Intectra at electrospray ionization (ESI). The reaction progress was monitored by TLC on Merck plates (Kieselgel 60 F_{254}). The chromatographic separation of reaction mixtures was performed on silica gel 40/60 (Kieselgel 60, Merck). Melting points were measured on a Koeffler heating block.

(22*R*,23*R*,24*S*)-23-Acetoxy-22-hydroxy-24-ethyl-5α-cholest-2-en-6-one (III). To a solution of 400 mg (0.98 mmol) of diol **I** in 8 ml of pyridine was added 0.5 ml (5 mmol) of acetic anhydride. The mixture was stirred and left standing for 24 h. The solution was treated with water, extracted with ethyl acetate, the extract was dried with anhydrous sodium sulfate, the solvent was evaporated. We obtained 500 mg of 22,23-diacetoxy derivative **II** that without further purification was dissolved in 5 ml (1.8 mmol) of 5% solution of K_2CO_3 in methanol. The reaction progress was monitored by TLC. After 3 h the solvent was distilled off in a vacuum, the products were extracted from the residue into ethyl acetate. The extract was washed with water, dried with Na_2SO_4, and evaporated. The residue was subjected to column chromatography on silica gel (eluent petroleum ether–

ethyl acetate, 20:1). We obtained 210 mg (53%) of initial 22,23-dihydroxy-24-ethyl-5α-cholest-2-en-6-one (**I**) and 150 mg (38%) of hydroxyacetate **III**, mp 188–190°C (MeOH). IR spectrum (film), ν, cm^{-1}: 3600 (OH), 1735, 1710 (C=O), 1260 (OAc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.70 s (3H, 18-Me), 0.73 s (3H, 19-Me), 0.86 d (3H, 26-Me, *J* 7 Hz), 0.95–0.99 m (9H, 21-, 27-, 29-Mε), 2.09 s (3H, COMe), 2.24 m (2H, $C^{17}H$ and $C^{25}H$), 2.35 d.d (2H, C^4H, J_1 4, J_2 12 Hz), 3.72 t (1H, $C^{22}H$, *J* 8.4 Hz), 5.14 d (1H, $C^{23}H$, *J* 8.8 Hz), 5.59 m (1H, C^2H), 5.69 m (1H, C^3H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 11.81 q, 12.00 q, 13.09 q, 13.63 q, 18.96 q, 19.66 t, 21.09 q, 21.27 t, 21.46 q, 21.85 t, 23.95 t, 27.75 t, 28.44 d, 37.59 d, 37.92 d, 39.49 t, 39.60 t, 40.17 s, 42.75 s, 45.53 d, 47.05 t, 52.43 d, 53.47 d, 53.97 d, 56.70 d, 74.26 d, 76.04 d, 124.63 d, 125.08 d, 172.71 s, 212.02 s.

(23*R*,24*S*)-23-Acetoxy-24-ethyl-5α-cholest-2-ene-6,22-dione (IV). To 40 mg (0.09 mmol) of hydroxyacetate **III** dissolved in 5 ml of anhydrous CH_2Cl_2 was added 200 mg (0.27 mmol) of Dess–Martin reagent. The reaction mixture was stirred for 24 h, then it was passed through a silica gel bed that was washed with dichloromethane. The combined dichloromethane solutions were washed with saturated solution of sodium carbonate and twice with water, and evaporated. We isolated 35 mg (88%) of compound **IV**, mp 178–181°C (petroleum ether–EtOAc). IR spectrum (film), ν, cm^{-1}: 1740 (C=O), 1720 (C=O), 1710 (C=O), 1250 (OAc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.696 s (3H, 18-Me), 0.704 s (3H, 19-Me), 0.84–0.88 m (6H, 26- and 29-Me), 1.04 d (3H, 27-Me, *J* 6 Hz), 1.22 d (3H, 21-Me, *J* 7 Hz), 2.10 s (3H, COMe), 5.28 s (1H, $C^{23}H$), 5.57 m (1H, C^2H), 5.56 m (1H, C^3H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 12.13 q, 12.36 q, 13.65 q, 17.40 q, 18.08 q, 19.49 t, 20.95 q, 21.17 t, 21.68 q, 21.83 t, 24.28 t, 27.71 t, 28.12 d, 37.78 d, 39.38 t, 39.44 t, 40.17 s, 42.76 s. 44.58 d, 45.15 d, 47.03 t, 50.78 d, 53.43 d, 53.94 d, 56.18 d, 76.64 d, 124.62 d, 125.06 d, 170.53 s, 209.46 s, 212.04 s.

(23*R*,24*S*)-23-Acetoxy-2α,3α-dihydroxy-24-ethyl-5α-cholestane-6,22-dione (V). A mixture of 50 mg (0.11 mmol) of olefin **IV**, 110 mg of $K_3[Fe(CN)_6]$, 45 mg of K_2CO_3, 35 mg (0.37 mmol) of methanesulfonamide, and 1 mg (0.0027 mmol) of $K_2OsO_4 \cdot 2H_2O$ was dissolved in 4 ml of a mixture *tert*-butanol–water, 1:1. The reaction mixture was stirred for 72 h at room temperature and then it was treated with a saturated solution of Na_2SO_3 and extracted with ethyl acetate. The extract was washed with water, dried with anhydrous sodium sulfate. On removing the solvent the residue was subjected to column chromatography on silica gel (eluent petroleum ether–ethyl acetate, 1:3). Yield 30 mg (60%), mp 207–210°C (petroleum ether–EtOAc). IR spectrum (film), ν, cm^{-1}: 3600 (OH), 1740 (C=O), 1720 (C=O), 1710 (C=O), 1250 (OAc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.69 s (3H, 18-Me), 0.76 s (3H, 19-Me), 0.84–0.9 m (6H, 26- and 29-Me), 1.03 d (3H, 27-Me, *J* 7 Hz), 1.21 d (3H, 21-Me, *J* 7 Hz), 2.11 s (3H, COMe), 2.65 m (1H, $C^{20}H$), br.d (1H, C^5H_α, *J* 12 Hz), 3.75 m (1H, C^2H), 4.05 m (1H, C^3H), 5.29 m (1H, $C^{23}H$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 12.22 q, 12.35 q, 13.70 q, 17.40 q, 18.08 q, 19.48 t, 20.95 q, 21.25 t, 21.68 q, 24.27 t, 26.44 t, 27.70 t, 28.11 d, 37.75 d, 39.290 t, 40.28 t, 42.72 s, 42.86 s, 43.56 d, 44.59 d, 45.15 d, 46.77 t, 50.75 d, 53.75 d, 56.08 d, 68.39 d, 68.45 d, 76.52 d, 170.63 s, 209.47 s, 212.29 s.

(23*R*,24*S*)-2α,3α,23-Trihydroxy-5α-cholestane-6,22-dione (VI). In 3 ml of methanol was dissolved 20 mg (0.0387 mmol) of acetoxyketone **V**, and 6.5 mg of K_2CO_3 in 0.5 ml of water was added. The mixture was stirred for 24 h at room temperature, then the solvent was removed, and the products were extracted from the residue with ethyl acetate. On removing the solvent the residue was subjected to column chromatography on silica gel (eluent ethyl acetate). Yield 16 mg (82%), mp 205–208°C (EtOAc). IR spectrum (KBr), ν, cm^{-1}: 3400, 3270 (OH), 1710 (C=O). ^1H NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 0.75 s (3H, 18-Me), 0.76 s (3H, 19-Me), 0.84 t (3H, 29-Me, *J* 7 Hz), 0.96 d (3H, 26-Me, *J* 6.4 Hz), 1.02 d (3H, 27-Me, *J* 7 Hz), 1.12 d (3H, 21-Me, *J* 7 Hz), 2.72 d.d (1H, C^5H_α, J_1 12, J_2 3 Hz), 2.92 m (1H, $C^{20}H$), 3.64 m (1H, C^2H), 3.94 m (1H, C^3H), 4.31 m (1H, $C^{23}H$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 11.27 q, 11.85 q, 12.54 q, 16.49 q, 18.16 q, 18.24 t, 20.20 q, 21.05 t, 23.76 t, 26.53 t, 27.34 t, 28.89 d, 29.27 d, 37.84 t, 39.44 s, 39.81 t, 41.99 d, 42.29 s, 42.90 d, 43.67 t, 50.86 d, 51.65 d, 53.87 d, 56.05 d, 67.91 d, 68.83 d, 75.62 d, 213.41 s, 216.97 s.

(22*R*,23*R*,24*S*)-22-Acetoxy-23-hydroxy-24-ethyl-5α-cholest-2-en-6-one (VII). To 25 mg (0.056 mmol) of a solution of hydroxyacetate **III** in 2 ml of AcOH was added 0.2 ml of $BF_3 \cdot Et_2O$, the mixture was brought to boiling and then cooled. The reaction mixture was diluted with ethyl acetate, twice washed with water, then with a solution of sodium carbonate, again with water, and evaporated. The residue was subjected to column chromatography on silica gel (eluent petroleum ether–ethyl acetate, 2:1). We obtained 11 mg (44%) of initial hydroxyacetate **III** and 12 mg (48%) of 22-acetoxy-23-hydroxy derivative **VII**, mp 183–185°C (MeOH). IR spectrum (film), ν, cm^{-1}: 3500 (OH), 1735 (C=O), 1720

(C=O), 1250 (OAC). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.69 s (3H, 18-Me), 0.71 s (3H, 19-Me), 0.92–1.10 m (12H, 21-, 26-, 27- and 29-Me), 2.11 s (3H, COMe), 3.83 m (1H, C^{23}H), 5.04 d (1H, C^{22}H, *J* 9 Hz), 5.57 m (1H, C^{2}H), 5.69 m (1H, C^{3}H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 11.85 q, 13.01 q, 13.56 q, 13.63 q, 18.84 t, 19.38 q, 21.21 q, 21.26 t, 21.30 q, 21.84 t, 23.94 t, 28.04 t, 28.99 d, 36.87 d, 37.84 d, 39.51 t, 39.65 t, 40.11 s, 42.81 s, 46.94 d, 46.99 t, 52.89 d, 53.52 d, 53.96 d, 56.78 d, 72.09 d, 78.21 d, 124.56 d, 125.14 d, 172.34 s, 211.86 s.

(22*R*,24*S*)-22-Acetoxy-24-ethyl-5α-cholest-2-ene-6,23-dione (VIII). By procedure described for compound **IV** from 80 mg (0.16 mmol) of alcohol **VII** was obtained 63 mg (82%) of ketone **VIII**, mp 180–183°C (petroleum ether–EtOAc). IR spectrum (film), ν, cm^{-1}: 1740 (C=O), 1720 (C=O), 1710 (C=O), 1260 (OAc). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.71 s (3H, 18-Me), 0.73 s (3H, 19-Me), 0.82–0.88 m (9H, 26-, 27- and 29-Me), 0.91 d (3H, 21-Me, *J* 7 Hz), 2.16 s (3H, COMe), 2.33–2.39 m (3H, C^{5}H$_\alpha$, C^{7}H$_\beta$ and C^{20}H), 5.18 d (1H, C^{22}H, *J* 1.1 Hz), 5.57 m (1H, C^{2}H), 5.67 m (1H, C^{3}H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 10.50 q, 11.83 q, 13.56 q, 13.80 q, 19.01 q, 20.77 q, 21.10 t, 21.401 t, 21.56 q, 21.73 t, 23.79 t, 26.89 d, 28.15 d, 29.74 t, 36.24 d, 37.74 d, 39.24 t, 39.41 t, 40.14 s, 42.66 s, 46.89 t, 52.48 d, 53.34 d, 55.07 d, 56.76 d, 80.81 d, 124.49 d, 125.10 d, 170.64 s, 209.55 s, 211.93 s.

(23*R*,24*S*)-22-Acetoxy-2α,3α-dandhydroxy-24-ethyl-5α-cholestane-6,23-dione (IX). By procedure described for compound **V** from 50 mg (0.1 mmol) of olefin **VIII** was obtained 34.6 mg (65%) of diol **IX**, mp 213–217°C (MeOH). IR spectrum (KBr), ν, cm^{-1}: 3350, 3250, 1740 (C=O), 1720 (C=O), 1710 (C=O), 1250 (OAc). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.73 s (3H, 18-Me), 0.76 s (3H, 19-Me), 0.83–0.89 m (9H, 21-, 27- and 29-Me), 0.91 d (3H, 26-Me, *J* 6 Hz), 2.17 s (3H, COMe), 2.72 d.d (1H, C^{5}H$_\alpha$, J_1 12, J_2 3 Hz), 3.77 m (1H, C^{2}H), 4.05 m (1H, C^{3}H), 5.19 d (1H, C^{22}H, *J* 1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 10.50 q, 11.91 q, 13.60 q, 13.77 q, 18.99 q, 20.78 q, 21.17 t, 21.39 t, 21.56 q, 23.79 t, 26.32 t, 26.89 d, 28.15 t, 36.22 d, 37.70 d, 39.14 t, 40.15 t, 42.68 s, 42.93 s, 46.65 t, 50.75 d, 52.41 d, 53.62 d, 55.07 d, 56.65 d, 68.26 d, 68.38 d, 80.78 d, 170.69 s, 209.63 s, 212.09 s.

(22*R*,24*S*)-2α,3α,22-Trihydroxy-24-ethyl-5α-cholestane-6,23-dione (X). By procedure described for compound **VI** from 70 mg (0.135 mmol) of 22-acetoxy derivative **IX** was obtained 43 mg (65%) of triol **X**, mp 204–206°C (MeOH). IR spectrum (KBr), ν, cm^{-1}: 3450 (OH), 1705 (C=O). ^{1}H NMR spectrum, ($CDCl_3$–CD_3OD), δ, ppm: 0.71 s (3H, 18-Me), 0.73 s (3H, 19-Me), 0.74 d (3H, 21-Me, *J* 7 Hz), 0.77 t (3H, 29-Me, *J* 7 Hz), 0.85 d (3H, 27-Me, *J* 6.5 Hz), 0.88 d (3H, 26-Me, *J* 7 Hz), 2.47 m (1H, C^{20}H), 2.68 d.d (1H, C^{5}H$_\alpha$, J_1 12, J_2 3 Hz), 3.3 m (1H, C^{24}H), 3.64 m (1H, C^{2}H), 3.94 q (1H, C^{3}H, *J* 3 Hz), 4.15 br.s (1H, C^{23}H, $J_{w/2}$ 3 Hz). ^{13}C NMR spectrum ($CDCl_3$–CD_3OD), δ, ppm: 10.575 q, 11.790 q, 12.574 q, 13.354 q, 18.829 q, 21.168 t, 21.392 q, 22.155 t, 23.826 t, 26.404 t, 27.294 d, 28.095 t, 37.706 d, 37.971 d, 39.214 t, 39.736 t, 42.661 s, 42.840 s, 46.575 t, 50.937 d, 52.465 d, 53.646 d, 54.692 d, 56.646 d, 67.944 d, 68.168 d, 79.194 d, 214.063 s, 216.610 s.

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