ISSN 1070-4280, Russian Journal of Organic Chemistry, 2013, Vol. 49, No. 12, pp. 1807–1811. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © R.G. Savchenko, S.A. Kostyleva, V.N. Odinokov, 2013, published in Zhurnal Organicheskoi Khimii, 2013, Vol. 49, No. 12, pp. 1825–1829.

Diastereospecific Conjugation of 24-Oxo-25,26,27-trinor Analogs of Ecdysteroids with L-Ascorbic Acid

R. G. Savchenko, S. A. Kostyleva, and V. N. Odinokov

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, pr. Oktyabrya 141, Ufa, 450075 Bashkortostan, Russia
e-mail: odinokov@anrb.ru

Received June 21, 2013

Abstract—Acid-catalyzed acetalization of 24-oxo-25,26,27-trinor analogs of ecdysteroids in the reaction with 2,3-di-*O*-benzylascorbic acid diastereospecifically gives the corresponding *S*-diastereoisomer with respect to the acetal chiral center.

DOI: 10.1134/S1070428013120166

Ecdysteroids are hormones responsible for moulting, metamorphosis, and diapause of insects and crustaceans. Ecdysteroids are also produced (and in higher amounts) by some plants, which makes it possible to isolate these structurally unique polyhydroxy sterols and explore their properties and chemical transformations [1–5]. Ecdysteroids are not toxic to warm-blooded animals and humans; moreover, they have diverse positive effects on the human organism [6]. An up-to-date approach to the design of new medical agents is based on conjugation of compounds whose biological activity is known. This may lead to synergistic effect or appearance of new biologically important properties. For example, a conjugate of ecdysteroid and α-tocopherol analog was shown [7] to be a potent antioxidant which inhibited lipid peroxidation more efficiently than did the initial 20-hydroxyecdysone and α-tocopherol; it also enhanced the activity of catalase and superoxide dismutase [8, 9]. In recent years, attention was given to conjugates of L-ascorbic acid (2,3-dehydro-L-gulonic acid γ-lactone, vitamin C); in particular, a conjugate of L-ascorbic acid with α-tocopherol turned out to be highly efficient in the protection of liver and myocardium cell membranes from free radical damage, and its efficiency exceeded that of α-tocopherol and ascorbic acid taken alone [10].

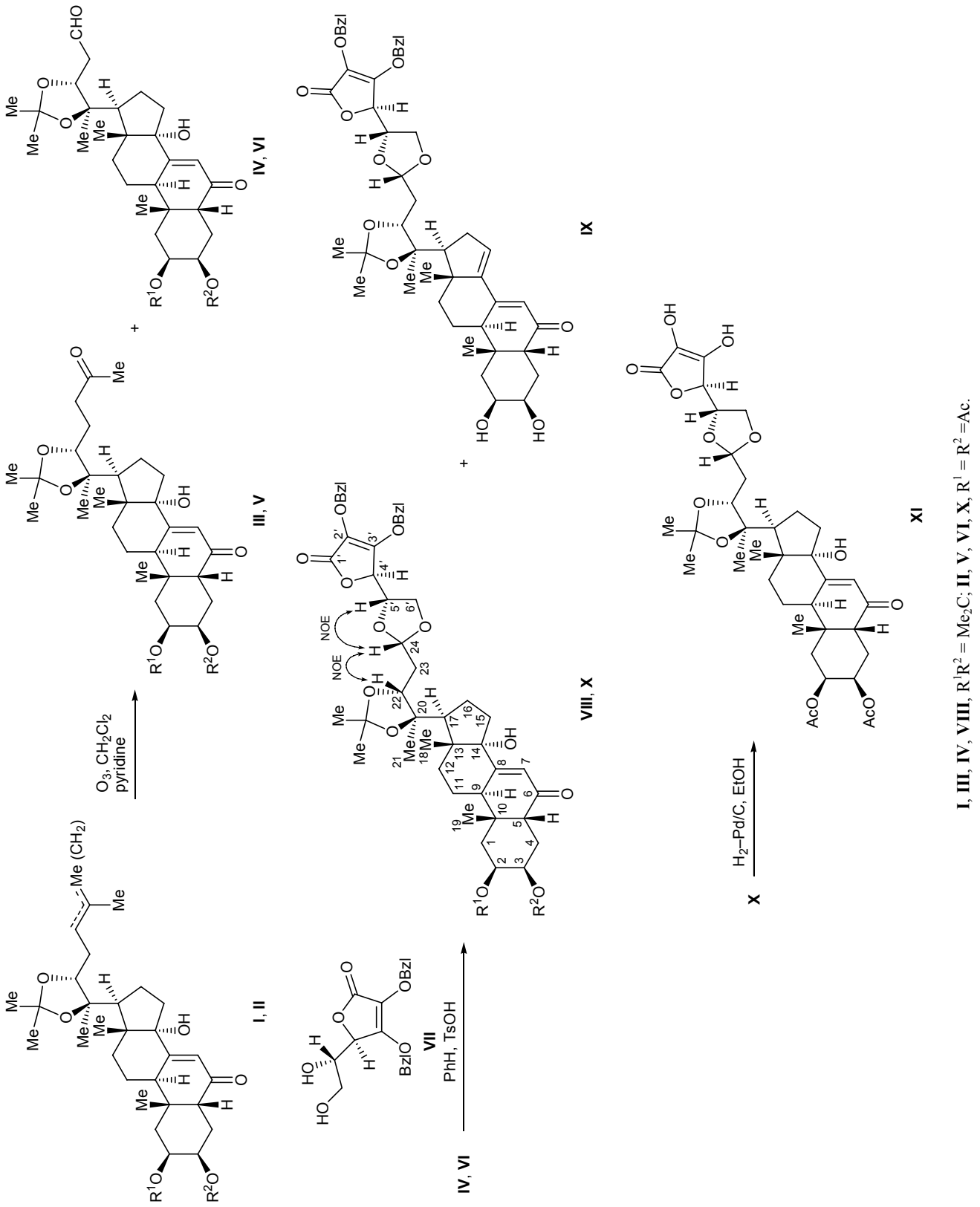
Ascorbic acid conjugates with ecdysteroids have not been reported previously. We were the first to synthesize such compounds. For this purpose, 24-oxo-25,26,27-trinorponasterone A 2,3:20,22-diacetonide (**IV**) and 2,3-di-*O*-acetyl-20,22-acetonide **VI** as mixtures with oxo derivatives **III** and **V** (obtained by ozonolysis of selectively protected ω-anhydro-20-hydroxyecdysones **I** and **II** [11, 12]) were brought into acid-catalyzed condensation with (4*R*,5*S*)-2,3-*O*-dibenzylascorbic acid (**VII**) prepared from commercially available L-(+)-ascorbic acid [13] (Scheme 1).

The reaction of equimolar amounts of diacetonide **IV** and compound **VII** in benzene in the presence of *p*-toluenesulfonic acid (TsOH) gave conjugate **VIII** (yield 15%) and its 2,3-deprotected 14,15-dehydrated derivative, compound **IX** (yield 23%). Relatively easy removal of 2,3-acetonide protection from ecdysteroid 2,3:20,22-diacetonides under acidic conditions and dehydration involving the 14α-hydroxy group were reported previously [7, 14, 15]. We succeeded in minimizing side processes by using 2,3-diacetyl protection instead of 2,3-acetonide. The condensation of aldehyde **VI** with compound **VII** under analogous conditions was more selective, and conjugate **X** was isolated in 48% yield.

The ^{1}H and ^{13}C NMR spectra of **VIII** and **X** contained signals typical of structural fragments of the initial ecdysteroids **IV** and **VI** and ascorbic acid derivative **VII**. Signals were assigned using homo- and heteronuclear correlation techniques (COSY, NOESY, HSQC, HMBC), as well as by comparing with the spectra of the initial compounds.

Compound **IX** displayed in the ^{13}C NMR spectrum only one signal (δ_C 106.63) assignable to quaternary acetal carbon atom, which confirmed deprotection of

Scheme 1.



I, **III**, **IV**, **VIII**, $R^1R^2 = Me_2C$; **II**, **V**, **VI**, **X**, $R^1 = R^2 = Ac$.

the 2,3-dihydroxy fragment (the ^{13}C NMR spectrum of 20-hydroxyecdysone diacetonide contains two signals at δ_C 106.68 and 108.20 ppm [16]). In the sp^2-carbon region we observed additional signals from disubstituted (δ_C 147.12 ppm) and monosubstituted (δ_C 120.30 ppm) double-bonded carbon atoms resulting from elimination of the 14α-hydroxy group. Analogous double bond is present in the molecules of stachysterone B derivatives [16].

The formation of conjugates is confirmed by the presence in the spectra of **VIII**–**X** of signals from tertiary acetal carbon atoms (C^{24}) in the region δ_C 101.4–103.5 ppm, which showed cross peaks with hydrogen atoms resonating at δ 5.12–5.14 ppm in the HSQC spectra (cf. [7, 10]). The structure of the obtained compounds was also confirmed by the MALDI TOF mass spectra.

The presence of only one C^{24} signal in the ^{13}C NMR spectra of **VIII**–**X** indicates configurational homogeneity of the newly formed acetal chiral center and hence stereospecificity of the conjugation of ω-formyl analogs of ecdysteroids with 2,3-*O*-dibenzylascorbic acid (**VII**). However, the condensation of racemic (6-benzyloxy-2,5,7,8-tetramethylchroman-2-yl)acetaldehyde at the vicinal hydroxy groups of ecdysteroids gave mixtures of diastereoisomers [7]. Presumably, stereospecific formation of acetals **VIII**–**X** is determined by spatial proximity of the aldehyde group to the homochiral C^{20} and C^{22} atoms in ecdysteroidal aldehydes **IV** and **VI**. The NOESY spectrum of **X** revealed coupling of the acetal proton ($C^{24}H$) with proton on $C^{5'}$ in the ascorbic acid fragment, which suggests *cis* orientation of these protons in the dioxolane ring and therefore *S* configuration of the new chiral center (C^{24}). The presence in the NOESY spectrum of a cross peak between 24-H and proton on C^{22} in the ecdysteroid fragment corresponds to more favorable conformation of molecule **X** with *anti* orientation of the dioxolane rings linked by methylene group.

Reductive debenzylation of **X** quantitatively afforded (5*R*)-3,4-dihydroxy-5-{(2*S*,4*S*)-2-[(20*R*,22*R*)-2β,3β-diacetoxy-14α-hydroxy-20,22-isopropylidenedioxy-6-oxo-24,25,26,27-tetranor-5β-cholest-7-en-23-yl]-1,3-dioxolan-4-yl}furan-2(5*H*)-one (**XI**).

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer at 400.13 and 100.62 MHz, respectively, using tetramethylsilane as internal reference. Standard homo- and heteronuclear COSY, HSQC, and HMBC techniques (Bruker) were applied. The mass spectra were obtained on a Bruker-Autoflex III spectrometer (MALDI TOF, positive ion detection) using 2,5-dihydroxybenzoic acid and α-cyano-4-hydroxycinnamic acid as matrices. The melting points were measured on a Boetius micro hot stage. The elemental compositions were determined on a Carlo Erba EA-1108 CHNS-O analyzer. Silica gel KSKG 100/200 was used for column chromatography. Analytical thin-layer chromatography was performed on Silufol plates; spots were visualized by treatment with a solution of vanillin in ethanol acidified with sulfuric acid.

(20*R*,22*R*)-14α-Hydroxy-2β,3β:20,22-bis(isopropylidenedioxy)-27-nor-5β-cholest-7-ene-6,25-dione (III) and (20*R*,22*R*)-14α-hydroxy-2β,3β:20,22-bis(isopropylidenedioxy)-6-oxo-25,26,27-trinor-5β-cholest-7-ene-24-al (IV). A solution of 0.3 g (0.55 mmol) of compound **I** in 6 mL of methylene chloride–pyridine (5:1) was cooled to 0°C, and an ozone/oxygen mixture was passed through the solution at a flow rate of 10 mL/min under vigorous stirring over a period of 3 min (until 0.55 mmol of O_3 was absorbed). The mixture was purged with argon and evaporated, and the residue was subjected to chromatography on 9 g of silica gel using chloroform–methanol (20:1) as eluent. We isolated 0.09 g (30%) of compound **III**, R_f 0.6 ($CHCl_3$–MeOH, 10:1), and 0.17 g (60%) of **IV**, R_f 0.5 ($CHCl_3$–MeOH, 10:1). The ^1H and ^{13}C NMR spectra of the products were identical to those given in [11].

(20*R*,22*R*)-2β,3β-Diacetoxy-14α-hydroxy-20,22-isopropylidenedioxy-27-nor-5β-cholest-7-ene-6,25-dione (V) and (20*R*,22*R*)-2β,3β-diacetoxy-14α-hydroxy-20,22-isopropylidenedioxy-6-oxo-25,26,27-trinor-5β-cholest-7-en-24-al (VI). An ozone/oxygen mixture was passed at a flow rate of 10 mL/min over a period of 3 min through a solution of 0.25 g (0.43 mmol) of compound **II** in 5 mL of methylene chloride–pyridine (5:1) under vigorous stirring at 0°C (until 0.43 mmol of O_3 was absorbed). The mixture was then treated as described above. We isolated 0.09 g (36%) of compound **V**, R_f 0.68 ($CHCl_3$–MeOH, 10:1), which was identical (in ^1H and ^{13}C NMR spectra) to a sample described in [12], and 0.12 g (50%) of compound **VI**, R_f 0.42 ($CHCl_3$–MeOH, 10:1), mp 165–166°C, $[\alpha]_D^{20}$ = +53.0° (*c* = 0.62, $CHCl_3$). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.78 s (3H, $C^{18}H_3$), 1.00 s (3H, $C^{19}H_3$), 1.15 s (3H, $C^{21}H_3$), 1.34 s and 1.40 s (3H each, 20,22-Me_2C), 1.48–2.68 m (16H,

CH, CH_2), 1.98 s and 2.09 s (3H each, MeCO), 2.35 d.d (1H, 5-H, J = 11.6, 5.6 Hz), 3.10 m (1H, 9-H, $w_{1/2}$ = 25.6 Hz), 4.19 m (1H, 22-H, $w_{1/2}$ = 10.8 Hz), 5.04 m (1H, 2-H, $w_{1/2}$ = 15.6 Hz), 5.30 br.s (1H, 3-H, $w_{1/2}$ = 9.6 Hz), 5.84 s (1H, 7-H), 9.79 br.s (1H, CHO, $w_{1/2}$ = 7.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.97 (C^{18}), 20.37 (C^{11}), 21.06 (**Me**CO), 21.12 (C^{16}), 22.12 (C^{21}), 23.80 (C^{19}), 26.88 (C^{15}), 28.80 and 29.09 (**Me**$_2$C), 30.81 (C^{12}), 31.46 (C^4), 33.60 (C^9), 33.93 (C^1), 38.30 (C^{10}), 43.20 (C^{23}), 47.15 (C^{13}), 50.91 (C^5), 48.88 (C^{17}), 67.03 (C^3), 68.67 (C^2), 75.43 (C^{22}), 84.05 (C^{20}), 84.43 (C^{14}), 121.47 (C^7), 107.97 (Me$_2$**C**), 164.83 (C^8), 170.28 and 170.59 (Me**C**O), 200.34 (C^{24}), 202.32 (C^6). Mass spectrum: m/z 583.309 $[M + Na]^+$. Found, %: C 66.41; H 7.89. $C_{31}H_{44}O_9$. Calculated, %: C 66.98; H 8.04.

(5*R*)-3,4-Dibenzyloxy-5-{(2*S*,4*S*)-2-[(20*R*,22*R*)-14α-hydroxy-2,3:20,22-bis(isopropylidenedioxy)-6-oxo-24,25,26,27-tetranor-5β-cholest-7-en-23-yl]-1,3-dioxolan-4-yl}furan-2(5*H*)-one (VIII) and (5*R*)-3,4-dibenzyloxy-5-{(2*S*,4*S*)-2-[(20*R*,22*R*)-2β,3β-dihydroxy-20,22-isopropylidenedioxy-6-oxo-24,25,26,27-tetranor-5β-cholesta-7,14-dien-23-yl]-1,3-dioxolan-4-yl}furan-2(5*H*)-one (IX). Aldehyde **IV**, 0.20 g (0.39 mmol), was dissolved in 3 mL of anhydrous benzene, 0.02 g of *p*-toluenesulfonic acid was added, the mixture was stirred for 20 min at room temperature, a solution of 0.14 g (0.39 mmol) of compound **VII** in 3 mL of anhydrous benzene was added, and the mixture was stirred for 24 h at room temperature (until the initial compounds disappeared according to the TLC data). The mixture was treated with 5 mL of water and 0.02 mL of a saturated solution of $NaHCO_3$ and extracted with ethyl acetate (3×15 mL), the extract was evaporated, and the residue was subjected to chromatography on 8.5 g of silica gel using chloroform as eluent. We isolated 0.05 g (15%) of compound **VIII**, R_f 0.5 ($CHCl_3$–MeOH, 10:1), and 0.07 g (23%) of **IX**, R_f 0.4 ($CHCl_3$–MeOH, 10:1).

Compound **VIII**. mp 99–101°C, $[\alpha]_D^{20}$ = 7.8° (c = 0.33, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.00 s (3H, $C^{18}H_3$), 1.23 s (3H, $C^{19}H_3$), 1.28 s (3H, $C^{21}H_3$), 1.35 s and 1.45 s (3H each, 20,22-Me$_2$C), 1.37 s and 1.43 s (3H each, 2,3-Me$_2$C), 1.52–2.67 m (18H, CH, CH_2), 4.00 m (1H, 22-H), 4.12 m (2H, 6′-H), 4.25 m (1H, 5′-H, $w_{1/2}$ = 27.6 Hz), 4.55 d (1H, 4′-H, J = 2.4 Hz), 4.72 m (1H, 3-H, $w_{1/2}$ = 14.8 Hz), 4.75 br.s (1H, 2-H, $w_{1/2}$ = 5.2 Hz), 5.12 m (1H, 24-H, $w_{1/2}$ = 11.6 Hz), 5.14 s (2H, 2′-OCH_2), 5.20 s (2H, 3′-OCH_2), 5.85 s (1H, 7-H), 7.22–7.40 m (10H, H_{arom}). Mass spectrum: m/z 893.674 $[M + K]^+$. Found, %: C 70.24; H 7.31. $C_{50}H_{62}O_{12}$. Calculated, %: C 69.98; H 7.84. M + K 893.387.

Compound **IX**. mp 134–136°C, $[\alpha]_D^{20}$ = –1.5° (c = 0.40, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.00 s (3H, $C^{18}H_3$), 1.22 s (3H, $C^{19}H_3$), 1.25 s (3H, $C^{21}H_3$), 1.34 s and 1.45 s (3H each, 20,22-Me$_2$C), 1.61–2.32 m (15H, CH, CH_2), 2.53 m (1H, 5-H, $w_{1/2}$ = 22.4 Hz), 3.18 m (1H, 9-H, $w_{1/2}$ = 9.2 Hz), 3.94 m (2H, 6′-H, 22-H), 4.04 m (2H, 3-H, 6′-H), 4.19 m (1H, 2-H, $w_{1/2}$ = 16.8 Hz), 4.57 m (1H, 5′-H, $w_{1/2}$ = 12.0 Hz), 4.72 d (1H, 4′-H, J = 2.4 Hz), 5.10 m (1H, 24-H, $w_{1/2}$ = 12.0 Hz), 5.12 s (2H, 2′-OCH_2), 5.20 s (2H, 3′-OCH_2), 5.26 m (1H, 15-H, $w_{1/2}$ = 5.6 Hz), 5.42 s (1H, 7-H), 7.23–7.39 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.73 (C^{18}), 20.50 (C^{11}), 21.77 (C^{21}), 26.15 and 28.30 (**Me**$_2$C), 27.44 (C^{12}), 28.10 (C^{19}), 34.24 (C^4), 35.78 (C^{16}), 37.67 (C^{23}), 37.90 (C^1, C^9), 42.23 (C^{10}), 45.13 (C^{13}), 52.33 (C^5), 55.10 (C^{17}), 68.14 (C^2, C^3), 69.11 ($C^{6'}$), 72.84 (3′-OCH_2), 73.06 (2′-OCH_2), 74.13 ($C^{5'}$), 75.18 ($C^{4'}$), 76.55 (C^{22}), 82.50 (C^{20}), 101.44 (C^{24}), 106.68 (Me$_2$**C**), 118.39 (C^7), 120.30 (C^{15}); 127.05, 127.89, 128.33 (C_6H_5); 134.49 ($C^{3'}$), 135.12 ($C^{2'}$), 147.12 (C^{14}), 156.37 (C^8), 172.00 ($C^{1'}$), 202.92 (C^6). Found, %: C 70.83; H 7.08. $C_{47}H_{56}O_{11}$. Calculated, %: C 70.21; H 7.79.

(5*R*)-3,4-Dibenzyloxy-5-{(2*S*,4*S*)-2-[(20*R*,22*R*)-2β,3β-diacetoxy-14α-hydroxy-20,22-isopropylidenedioxy-6-oxo-24,25,26,27-tetranor-5β-cholest-7-en-23-yl]-1,3-di-oxolan-4-yl}furan-2(5*H*)-one (X). Aldehyde **VI**, 0.17 g (0.3 mmol), was dissolved in 3 mL of anhydrous benzene, 0.02 g of *p*-toluenesulfonic acid was added, the mixture was stirred for 20 min at room temperature, 0.11 g (0.3 mmol) of compound **VII** in 3 mL of anhydrous benzene was added, and the mixture was stirred for 24 h at room temperature (until the initial compounds disappeared according to the TLC data). The mixture was then treated as described above for the reaction with aldehyde **IV**. Yield 0.13 g (48%), R_f 0.5 ($CHCl_3$–MeOH, 10:1), mp 119–121°C, $[\alpha]_D^{20}$ = +60.3° (c = 0.71, $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.80 s (3H, $C^{18}H_3$), 1.04 s (3H, $C^{19}H_3$), 1.14 s (3H, $C^{21}H_3$), 1.34 s and 1.41 s (3H each, 20,22-Me$_2$C), 1.63 m and 1.80 m (2H, 11-H), 1.67 m and 1.92 m (2H, 1-H), 1.83–2.05 (11H, CH, CH_2), 2.12 s and 2.18 s (3H each, MeCO), 2.23 m (1H, 17-H, $w_{1/2}$ = 7.6 Hz), 2.41 d.d (1H, 5-H, J = 12.8, 4.0 Hz), 3.12 m (1H, 9-H, $w_{1/2}$ = 23.2 Hz), 3.92 m (1H, 22-H), 3.94 m and 4.08 m (2H, 6′-H), 4.23 m (1H, 5′-H), 4.60 d (1H, 4′-H, J = 3.6 Hz), 5.14 m (1H, 24-H, $w_{1/2}$ = 7.6 Hz), 5.16 m (1H, 2-H, $w_{1/2}$ = 6.8 Hz), 5.18 s (2H, 2′-OCH_2), 5.20 s (2H, 3′-OCH_2), 5.38 br.s (1H, 3-H, $w_{1/2}$ =

11.2 Hz), 5.84 s (1H, 7-H), 7.22–7.39 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.06 (C^{18}), 20.37 (C^{11}), 20.90 and 21.11 (**Me**CO), 21.90 (C^{21}, C^{16}), 23.85 (C^{19}), 26.92 and 28.92 (**Me**$_2$C), 29.68 (C^{15}), 30.80 (C^4), 31.56 (C^{12}), 33.57 (C^{23}), 33.64 (C^9), 34.02 (C^1), 38.38 (C^{10}), 47.20 (C^{13}), 48.72 (C^{17}), 51.01 (C^5), 65.96 ($C^{6'}$), 67.06 (C^3), 68.68 (C^2), 73.64 (2′-OCH_2), 73.88 (3′-OCH_2), 74.16 ($C^{5'}$), 74.97 ($C^{4'}$), 76.85 (C^{22}), 84.21 (C^{20}), 84.67 (C^{14}), 103.48 (C^{24}), 107.44 (Me_2**C**), 121.47 (C^7, $C^{2'}$); 127.77, 128.66, 128.71, 129.11 (C_6H_5); 156.40 ($C^{3'}$), 164.79 (C^8), 168.98 ($C^{1'}$), 170.19 and 170.39 (Me**C**O), 202.26 (C^6). Mass spectrum, *m/z*: 921.401 $[M + Na]^+$, 937.394 $[M + K]^+$. Found, %: C 68.13; H 6.95. $C_{51}H_{62}O_{14}$. Calculated, %: C 68.48; H 7.09. *M* + Na 921.403, *M* + K 937.377.

(5*R*)-3,4-Dihydroxy-5-{(2*S*,4*S*)-2-[(20*R*,22*R*)-2β,3β-diacetoxy-14α-hydroxy-20,22-isopropylidenedioxy-6-oxo-24,25,26,27-tetranor-5β-cholest-7-en-23-yl]-1,3-di-oxolan-4-yl}furan-2(5*H*)-one (XI). Hydrogen was passed over a period of ~3 h through a suspension of 0.13 g (0.14 mmol) of compound **X** and 0.04 g of 10% Pd/C in 5 mL of anhydrous ethanol, the progress of the reaction being monitored by TLC. The catalyst was filtered off, the filtrate was evaporated, and the residue was purified by chromatography on silica gel (4 g) using chloroform as eluent. Yield 0.09 g (90%), R_f 0.4 ($CHCl_3$–MeOH, 5:1), mp 225–226°C, $[\alpha]_D^{20}$ = +21.0° (*c* = 0.41, MeOH). ^1H NMR spectrum (CD_3OD), δ, ppm: 0.85 s (3H, $C^{18}H_3$), 1.04 s (3H, $C^{19}H_3$), 1.20 s (3H, $C^{21}H_3$), 1.34 s and 1.42 s (3H each, 20,22-Me_2C), 1.56–1.85 (17H, CH, CH_2), 2.00 s and 2.13 s (3H each, MeCO), 2.33 m (1H, 17-H, $w_{1/2}$ = 10.4 Hz), 2.36 m (1H, 5-H, $w_{1/2}$ = 7.2 Hz), 3.37 m (1H, 9-H, $w_{1/2}$ = 14.8 Hz), 3.95 m (1H, 22-H), 3.97 m and 4.07 m (2H, 6′-H), 4.35 m (1H, 5′-H), 4.80 m (1H, 4′-H), 5.04 m (1H, 24-H, $w_{1/2}$ = 11.6 Hz), 5.11 m (1H, 2-H, $w_{1/2}$ = 7.2 Hz), 5.14 m (1H, 3-H, $w_{1/2}$ = 7.2 Hz), 5.87 s (1H, 7-H). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 16.26 (C^{18}), 19.54 (C^{19}), 20.16 (C^{11}), 20.93 (C^{21}), 21.20 (C^{16}), 22.42 and 22.82 (**Me**CO), 25.85 and 27.90 (**Me**$_2$C), 28.80 (C^{12}), 30.32 (C^4), 31.20 (C^{15}), 33.73 (C^{23}), 37.53 (C^9), 37.80 (C^{10}), 37.89 (C^1), 47.50 (C^{13}), 49.00 (C^{17}), 51.05 (C^5), 67.29 (C^3), 68.15 ($C^{6'}$), 68.72 (C^2), 74.20 ($C^{5'}$), 75.90 ($C^{4'}$), 77.28 (C^{22}), 84.19 (C^{20}), 84.33 (C^{14}), 102.44 (C^{24}), 107.25 (Me_2**C**), 120.64 ($C^{3'}$), 121.40 (C^7), 156.20 ($C^{2'}$), 164.20 (C^8), 170.61 and 170.81 (Me**C**O), 179.86 ($C^{1'}$), 203.00 (C^6). Mass spectrum: *m/z* 723.463 $[M - H_2O + Na]^+$. Found, %: C 61.83; H 7.01. $C_{37}H_{50}O_{14}$. Calculated, %: C 61.28; H 7.69. *M* – H_2O + Na 723.309.

REFERENCES

1. Akhrem, A.A. and Kovganko, N.V., *Ekdisteroidy. Khimiya i biologicheskaya aktivnost'* (Ecdysteroids. Chemistry and Biological Activity), Minsk: Nauka i tekhnika, 1989, p. 325.
2. Kovganko, N.V., *Khim. Prirodn. Soedin*., 1997, p. 655.
3. Drach, S.V., Khripach, V.A., Litvinovskaya, R.P., Lyakhov, A.S., Schneider, B., and Zhylitskaya, H.A., *Steroids*, 2010, vol. 75, p. 184.
4. Odinokov, V.N., *Izv. Akad. Nauk, Ser. Khim*., 2012, p. 1375.
5. Ves'kina, N.A. and Odinokov, V.N., *Russ. J. Org. Chem*., 2012, vol. 48, p. 1137.
6. Dinan, L., *Phytochemistry*, 2001, vol. 57, p. 325.
7. Savchenko, R.G., Urazaeva, Ya.R., Spivak, A.Yu., and Odinokov, V.N., *Russ. J. Org. Chem*., 2010, vol. 46, p. 1157.
8. Khairullina, V.R., Urazaeva, Ya.R., Savchenko, R.G., Gerchikov, A.Ya., and Odinokov, V.N., *Kinet. Katal*., 2010, vol. 51, p. 528.
9. Odinokov, V.N., Savchenko, R.G., Urazaeva, Ya.R., Syrov, V.N., Afon'kina, S.R., Khushbaktova, Z.A., and Tsaruk, A.V., Russian Patent no. 2490267, 2013; *Byull. Izobret*., 2013, no. 23.
10. Manfredini, S., Vertuani, S., Manfredi, B., Rossoni, G., Calviello, G., and Palozza, P., *Bioorg. Med. Chem*., 2000, vol. 8, p. 2791.
11. 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.
12. Odinokov, V.N., Savchenko, R.G., Afon'kina, S.R., and Khalilov, L.M., *Russ. J. Org. Chem*., 2005, vol. 41, p. 376.
13. Kato, K., Terao, S., Shimamoto, N., and Hirata, M., *J. Med. Chem*., 1988, vol. 31, p. 793.
14. Politova, N.K., Punegov, V.V., Volodin, V.V., and Ignatov, A.V., *Khim. Prirodn. Soedin*., 1997, p. 74.
15. Galyautdinov, I.V., Nazmeeva, S.R., Savchenko, R.G., Ves'kina, N.A., Nedopekin, D.V., Fatykhov, A.A., Khalilov, L.M., and Odinokov, V.N., *Russ. J. Org. Chem*., 2004, vol. 40, p. 675.
16. Odinokov, V.N., Galyautdinov, I.V., Nedopekin, D.V., and Khalilov, L.M., *Izv. Akad. Nauk, Ser. Khim*., 2003, p. 220.