ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 8, pp. 1157–1161. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © R.G. Savchenko, Ya.R. Urazaeva, A.Yu. Spivak, V.N. Odinokov, 2010, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 8, pp. 1158–1161.

(6-Benzyloxy-2,5,7,8-tetramethylchroman-2-yl)acetaldehyde Conjugates with 20-Hydroxyecdysone, Stachysterone B, and Their 20,22-Acetonides

R. G. Savchenko, Ya. R. Urazaeva, A. Yu. Spivak, and V. N. Odinokov

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

Received July 17, 2009

Abstract—Conjugates consisting of ecdysteroid and α-tocopherol analog fragments were synthesized for the first time from 20-hydroxyecdysone and (6-benzyloxy-2,5,7,8-tetramethylchroman-2-yl)acetaldehyde.

DOI: 10.1134/S1070428010080075

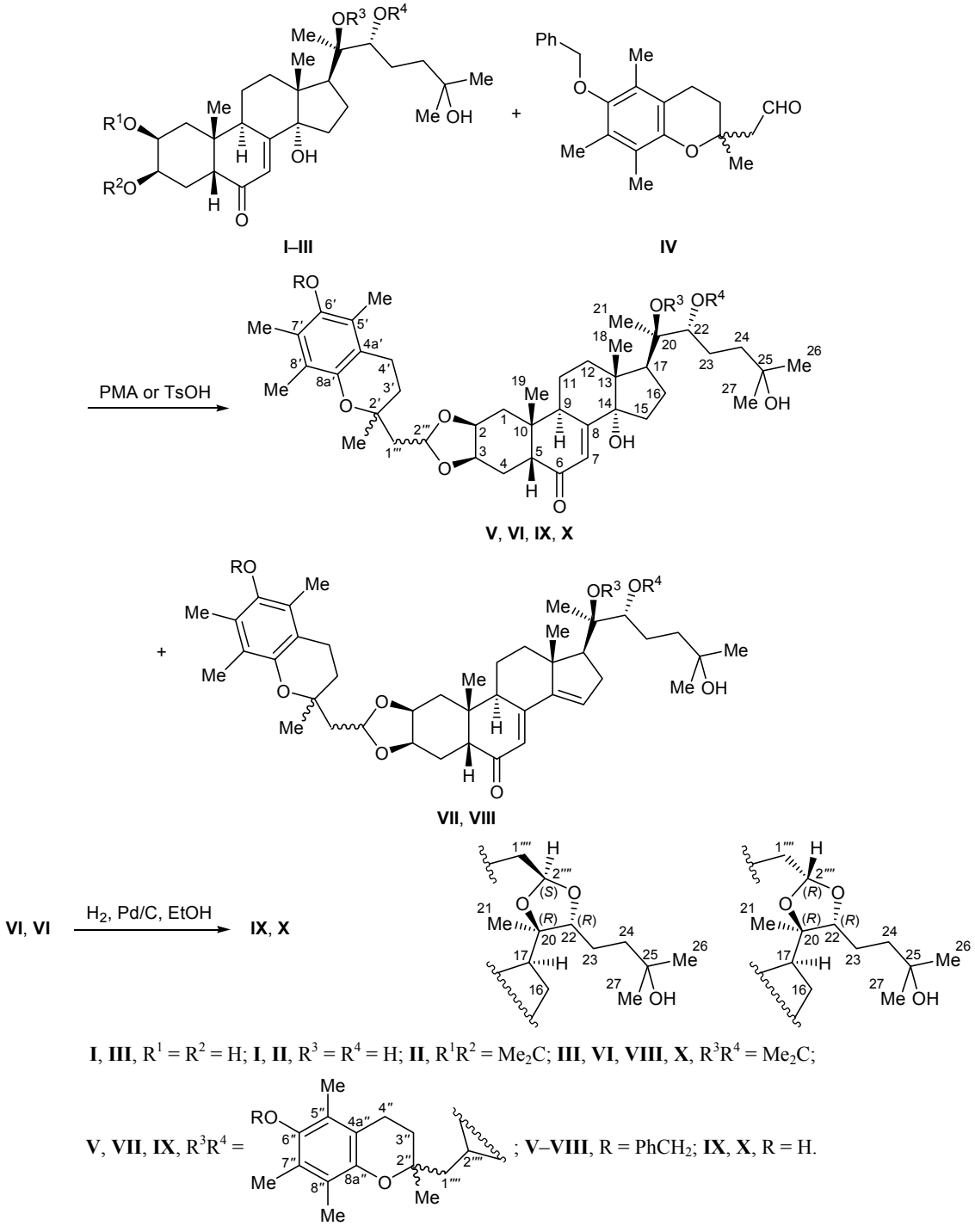
Ecdysteroids (insect ecdysis, metamorphosis, and diapause hormones) are present not only in insect organisms, but also (in considerably higher concentrations) in plants from which these unique polyhydroxylated sterols were isolated. The properties and some chemical transformations of ecdysteroids were studied [1, 2]. It was found that ecdysteroids are nontoxic for warm-blooded animals. Versatile physiological effect of ecdysteroids on humans and animals was revealed: they were found to control mineral, carbohydrate, lipid, and protein exchange, normalize sugar and cholesterol concentration in blood, stimulate hemopoietic activity, and exert immunomodulatory effect [3]. The diversity of physiological action of ecdysteroids is determined to some extent by their antioxidant properties, for many diseases are related to oxidative stress [4].

We believed that a promising way of enhancing pharmacological effect of ecdysteroids may be conjugation with natural phenolic antioxidants such as α-tocopherol and its analogs. For this purpose, we examined reactions of 20-hydroxyecdysone (**I**) and its 2,3- and 20,22-acetonides **II** and **III** with (6-benzyloxy-2,5,7,8-tetramethylchroman-2-yl)acetaldehyde (**IV**). The reaction of ecdysteroid **I** with 2 equiv of aldehyde **IV**, catalyzed by phosphomolybdic acid (PMA), gave 62% of the corresponding bis-adduct **V** (Scheme 1). This reaction occurred at a higher rate in the presence of *p*-toluenesulfonic acid as catalyst, but the yield of bis-acetal **V** did not change. Bis-adduct **V** was also formed in the reaction of 20-hydroxyecdysone 2,3-acetonide (**II**) with an equimolar amount of aldehyde **IV** in the presence of TsOH or PMA, but the yield was lower (35%). Under analogous conditions, from 20,22-acetonide **III** we obtained 60% of 2,3-adduct **VI**. Presumably, the formation of bis-adduct **V** from 2,3-acetonide **II** is favored due to known lability of compound **II** in acid medium [1].

Apart from 20-hydroxyecdysone conjugates **V** and **VI**, from the reaction mixtures we isolated the corresponding 14,15-anhydro derivatives **VII** and **VIII** in 26 and 20% yield, respectively. Compounds **VII** and **VIII** can be regarded as analogous stachysterone B conjugates. 20-Hydroxyecdysone conjugates **V** and **VI** were subjected to debenzylation by hydrogenation over Pd/C in ethanol solution. As a result, the corresponding hydroxy derivatives **IX** and **X** were smoothly formed. The MALDI-TOF mass spectrum of bis-adduct **IX** contained $[M + H]^+$ ion peak. In the ^1H and ^{13}C NMR spectra of compounds **V**–**X** we observed signals from all protons iand carbon nuclei in the ecdysteroid and chroman fragments, in keeping with the assumed structure of their molecules.

Monoadduct **VI** displayed in the ^{13}C NMR spectrum (in the region typical of acetal carbon atoms) signals from quaternary (δ_C 106.97 ppm) and tertiary (δ_C 101.97 ppm) carbon atoms in the 20,22-*O*-isopropylidene (cf. [5]) and ethylidenedioxy groups (cf. [6]), respectively. The ^{13}C NMR spectrum of bis-adduct **V** contained three signals from carbon atoms in the ethylidenedioxy groups at δ_C 101.99, 101.41, and 101.63 ppm with an intensity ratio of 2:1:1. Obvi-

Scheme 1.



I, **III**, $R^1 = R^2 = H$; **I**, **II**, $R^3 = R^4 = H$; **II**, $R^1R^2 = Me_2C$; **III**, **VI**, **VIII**, **X**, $R^3R^4 = Me_2C$;

V, **VII**, **IX**, R^3R^4 = ; **V**–**VIII**, R = $PhCH_2$; **IX**, **X**, R = H.

ously, the two latter signals correspond to the 20,22-*O*-(6-benzyloxy-2,5,7,8-tetramethylchroman-2-yl)ethylidene fragment.

The formation of 1,3-dioxolane derivatives, i.e., cyclic 2,3- and 20,22-acetals, involves appearance of two new asymmetric centers, the $C^{2'''}$ and $C^{2''''}$ atoms in **V**. Among these, only the latter ($C^{2''''}$) gives two signals as a result of formation of (*S*,*R*,*R*)- and (*R*,*R*,*R*)-diastereoisomers. Obviously, the $C^{2''''}$ signal is doubled due to the presence of strongly different substituents on C^{20} and C^{22} in the 1,3-dioxolane ring of 20,22-acetal. On the other hand, the substituents on C^2 and C^3 in the 1,3-dioxolane ring of the 2,3-acetal moiety differ only slightly, and the $C^{2'''}$ chiral acetal carbon atom

gives only one peak in the ^{13}C NMR spectrum. Protons at the $C^{2'''}$ and $C^{2''''}$ acetal carbon atoms in **V** resonated in the ^1H NMR spectrum as broadened singlets ($w_{1/2}$ = 13 Hz) at δ 5.18 (20,22) and 5.24 ppm (2,3).

In the ^{13}C NMR spectrum of compound **VIII**, instead of signals at δ_C ~30.86 (C^{15}) and 84.86 ppm (C^{14}), we observed signals typical of sp^2-hybridized carbon atoms at δ ~122.98 (C^{14}) and 148.75 ppm (C^{15}). The ^1H NMR spectra of **VII** and **VIII** displayed an additional signal at δ ~6.0 ppm (15-H) (apart from the 7-H signal at δ ~6.1 ppm). These findings reflected formation of double C^{14}=C^{15} bond in stachysterone B conjugates **VII** and **VIII** (cf. [5]).

To conclude, we were the first to synthesize ecdysteroid conjugates with α-tocopherol analog at the ω-aldehyde group of the latter.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker Avance-400 instrument at 400.13 and 100.62 MHz, respectively. Signals were assigned with the use of homo- and heteronuclear correlation techniques (DEPT-135, COSY, HSQC, HMBC). The chemical shifts were determined relative to tetramethylsilane as internal reference. The mass spectrum of compound **IX** was obtained on a Bruker Autoflex III instrument (MALDI TOF, positive ion detection). The melting points were determined on a Boetius melting point apparatus. The optical rotations were measured on a Perkin–Elmer-141 polarimeter. The purity of the products was checked by TLC on Silufol plates; spots were developed by treatment with a solution of vanillin in ethanol acidified with sulfuric acid.

2,3:20,22-Bis-*O*-[2-(6-benzyloxy-2,5,7,8-tetramethylchroman-2-yl)ethylidene]-20-hydroxyecdysone (V) and 2,3:20,22-bis-*O*-[2-(6-benzyloxy-2,5,7,8-tetramethylchroman-2-yl)ethylidene]stachysterone B (VII). *a*. A solution of 0.28 g (0.83 mmol) of aldehyde **IV** in 3 ml of ethyl acetate was added to a solution of 0.20 g (0.42 mmol) of compound **I** in 3 ml of ethyl acetate, 0.02 g of *p*-toluenesulfonic acid was added, and the mixture was stirred for 24 h at room temperature and evaporated. The residue was subjected to column chromatography on silica gel (20 g) using chloroform as eluent.

Compound **V**. Yield 0.29 g (62%), R_f 0.56 ($CHCl_3$–MeOH, 20 : 1), mp 128–130°C, $[\alpha]_D^{20}$ = +20.7° (*c* = 2.03, $CHCl_3$). ^1H NMR spectrum, δ, ppm: 0.90 s (3H, $C^{18}H_3$), 1.00 s (3H, $C^{19}H_3$), 1.17 s (3H, $C^{21}H_3$), 1.27 s (3H, $C^{26}H_3$), 1.28 s (3H, $C^{27}H_3$), 1.37 s (6H, 2′-CH_3, 2″-CH_3); 2.11 s, 2.18 s, and 2.24 s (6H each, CH_3); 2.63 m (4H, 4′-H, 4″-H), 3.62 m (1H, 22-H), 4.10 m (1H, 2-H), 4.14 m (1H, 3-H), 4.71 s (4H, OC**H**$_2$Ph), 5.18 br.s (1H, 2‴-H), 5.24 br.s (1H, 2‴-H), 5.85 s (1H, 7-H), 7.35–7.50 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 11.92, 12.01, and 12.89 (6C, Me); 17.00 (C^{18}), 20.56 (C^{19}), 20.56 ($C^{4'}$, $C^{4''}$), 21.50 (C^{11}), 23.04 (C^{16}), 23.61 (C^{21}), 24.80 (2′-Me), 24.97 (2″-Me), 26.68 (C^{23}), 29.47 (C^{26}, C^{27}), 30.86 (C^{15}), 30.94 (C^4), 31.74 ($C^{3'}$), 31.85 ($C^{3''}$) 34.00 (C^{12}), 34.71 (C^9), 37.82 (C^1), 38.40 (C^{10}), 41.41 (C^{24}), 45.53 (C^{13}), 47.36 (C^5), 49.74 ($C^{1'''}$, C^{17}), 50.83 ($C^{1''''}$), 70.48 (C^{25}), 73.36 ($C^{2'}$, $C^{2''}$), 74.75 (O**C**H_2Ph), 76.75 (C^3), 77.07 (C^2), 83.55 (C^{20}), 83.85 (C^{22}), 84.86 (C^{14}), 101.41 and 101.63 ($C^{2''''}$), 101.99 ($C^{2'''}$), 117.41 ($C^{8a'}$), 117.49 ($C^{8a''}$), 121.43 (C^7), 123.04 ($C^{8'}$, $C^{8''}$), 126.06 ($C^{7'}$, $C^{7''}$), 127.74, 127.76 and 128.47 (Ph), 128.06 ($C^{5'}$, $C^{5''}$), 137.97 (OCH_2**C**), 147.48 ($C^{4a'}$), 147.60 ($C^{4a''}$), 148.39 ($C^{6'}$, $C^{6''}$), 163.23 (C^8), 202.62 (C^6). Found, %: C 75.95; H 7.99. $C_{71}H_{92}O_{11}$. Calculated, %: C 76.04; H 8.27.

Compound **VII**. Yield 0.12 g (26%), mp 124–125°C, $[\alpha]_D^{20}$ = –3.4° (*c* = 1.37, $CHCl_3$). ^1H NMR spectrum, δ, ppm: 0.80 s (3H, $C^{18}H_3$), 0.97 s (3H, $C^{19}H_3$), 1.14 s (3H, $C^{21}H_3$), 1.26 s (6H, $C^{26}H_3$, $C^{27}H_3$), 1.35 s (6H, 2′-CH_3, 2″-CH_3); 2.09 s, 2.18 s, and 2.22 s (6H each, CH_3); 2.62 m (4H, 4′-H, 4″-H), 3.66 m (1H, C^{22}), 4.12 m (1H, 2-H), 4.30 m (1H, 3-H), 4.69 s (4H, OC**H**$_2$Ph), 5.12 br.s (1H, 2‴-H), 5.23 br.s. (1H, 2‴-H), 5.98 br.s (1H, 15-H), 6.10 s (1H, 7-H), 7.20–7.51 m (10H, H_{arom}).

b. A solution of 0.28 g (0.83 mmol) of aldehyde **IV** in 3 ml of ethyl acetate was added to a solution of 0.20 g (0.42 mmol) of compound **I** in 3 ml of ethyl acetate, 0.02 g of phosphomolybdic acid was added, and the mixture was stirred for 54 h at room temperature and evaporated. The mixture was then treated as described above in *a* to isolate 0.29 g (61%) of compound **V** and 0.12 g (25%) of **VII**.

c. A solution of 0.13 g (0.38 mmol) of aldehyde **IV** in 3 ml of ethyl acetate was added to a solution of 0.20 g (0.38 mmol) of compound **II** in 3 ml of ethyl acetate, 0.02 g of *p*-toluenesulfonic acid was added, and the mixture was stirred for 24 h at room temperature and evaporated. The subsequent procedure was the same as that described above in *a*. We isolated 0.13 g (30%) of compound **V** and 0.07 g (15%) of **VII**.

2,3-*O*-[2-(6-Benzyloxy-2,5,7,8-tetramethylchroman-2-yl)ethylidene]-20,22-*O*-isopropylidene-20-hydroxyecdysone (VI) and 2,3-*O*-[2-(6-benzyloxy-

2,5,7,8-tetramethylchroman-2-yl)ethylidene]-20,22-*O*-isopropylidenestachysterone B (VIII). A solution of 0.08 g (0.24 mmol) of aldehyde **IV** in 2 ml of methylene chloride was added to a solution of 0.24 g (0.46 mmol) of compound **III** in 5 ml of methylene chloride, 0.02 g of phosphomolybdic acid was added, and the mixture was stirred for 48 h at room temperature and evaporated. The residue was subjected to chromatography on silica gel (20 g) using chloroform as eluent to isolate 0.24 g (60%) of compound **VI**, R_f 0.53 ($CHCl_3$–MeOH, 20:1) and 0.08 g (20%) of **VIII**, R_f 0.58 ($CHCl_3$–MeOH, 30:1).

Compound **VI**. mp 138–140°C, $[\alpha]_D^{20}$ = +19.3° (*c* = 1.77, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 0.80 s (3H, $C^{19}H_3$), 0.97 s (3H, $C^{18}H_3$), 1.18 s (3H, $C^{21}H_3$), 1.24 s (6H, $C^{26}H_3$, $C^{27}H_3$), 1.34 s and 1.36 s [3H each, $(CH_3)_2C$], 1.43 s (3H, 2′-CH_3); 2.11 s, 2.17 s, and 2.25 s (3H each, CH_3); 2.61 s (2H, 4′-H), 3.65 d (1H, 22-H, *J* = 8.0 Hz), 4.13 m (1H, 2-H), 4.17 m (1H, 3-H), 4.69 s (2H, OC**H**$_2$Ph), 5.22 br.s (1H, 2‴-H), 5.82 s (1H, 7-H), 7.35–7.50 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 11.93, 12.01, and 12.89 (CH_3); 17.04 (C^{18}), 20.58 ($C^{4'}$, C^{19}), 21.21 (C^{11}), 21.92 (C^{16}), 23.61 (C^{21}), 24.54 (C^{23}), 24.76 (2′-CH_3), 26.90 and 29.00 [(**C**H_3)$_2$C], 29.23 (C^{26}), 29.66 (C^{27}), 30.97 (C^{15}), 31.60 (C^4), 31.85 ($C^{3'}$), 34.77 (C^{12}, C^9), 37.75 (C^1), 38.35 (C^{10}), 41.39 (C^{24}), 45.52 (C^{13}), 47.49 (C^5), 49.02 (C^{17}), 50.09 ($C^{1'''}$), 70.37 (C^{25}), 73.15 ($C^{2'}$), 74.76 (O**C**H_2Ph), 77.44 (C^3), 77.33 (C^2), 82.01 (C^{22}), 84.44 (C^{20}), 84.74 (C^{14}), 101.97 ($C^{2'''}$), 117.05 ($C^{8a'}$), 121.24 (C^7), 123.03 ($C^{8'}$), 126.06 ($C^{7'}$), 127.77 ($C^{5'}$), 127.80 and 128.47 (C_{arom}), 137.95 (OCH_2**C**), 147.45 ($C^{4a'}$), 148.36 ($C^{6'}$), 163.44 (C^8), 202.62 (C^6). Found, %: C 74.00; H 9.01. $C_{52}H_{72}O_9$. Calculated, %: C 74.25; H 8.63.

Compound **VIII**. mp 129–131°C. ^{1}H NMR spectrum, δ, ppm: 0.98 s (3H, $C^{19}H_3$), 1.08 s (3H, $C^{18}H_3$), 1.23 s (3H, $C^{21}H_3$), 1.25 s (6H, $C^{26}H_3$, $C^{27}H_3$), 1.33 s and 1.36 s [6H, $(CH_3)_2C$], 1.45 s (3H, 2′-CH_3); 2.11 s, 2.18 s, and 2.23 s (3H each, CH_3); 2.63 m (2H, 4′-H), 3.73 d (1H, 22-H, *J* = 8.8 Hz), 4.08 m (1H, 2-H), 4.12 m (1H, 3-H), 4.70 s (2H, OC**H**$_2$Ph), 5.17 m (1H, 2‴-H), 5.95 (1H, 15-H), 6.11 s (1H, 7-H), 7.35–7.50 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 11.90, 11.99, and 12.86 (CH_3); 19.13 (C^{18}), 20.41 ($C^{4'}$), 20.58 (C^{11}), 22.64 (C^{21}), 23.24 (C^4), 23.73 (C^{23}), 24.76 and 24.83 (2′-CH_3), 27.35 (C^{19}), 29.23 (C^{26}), 29.66 (C^{27}), 29.70 [(**C**H_3)$_2$C], 31.62 (C^{12}), 31.97 ($C^{3'}$), 38.35 (C^{10}), 38.54 (C^9), 38.95 (C^{16}), 39.59 (C^{24}), 41.24 (C^1), 45.37 and 45.51 ($C^{1'''}$), 47.52 (C^{13}), 50.74 (C^5), 57.57 (C^{17}), 70.92 (C^{25}), 73.62 and 73.99 ($C^{2'}$), 74.76 (O**C**H_2C), 76.73 (C^3), 77.04 (C^2), 81.72 (C^{22}), 83.33 (C^{20}), 117.40 ($C^{8'}$), 122.98 (C^{14}), 128.46 (C^{15}), 101.99 ($C^{2'''}$), 117.05 ($C^{8a'}$), 121.31 (C^7), 120.72 ($C^{7'}$); 126.03, 126.07, and 128.46 (C_{arom}); 128.09 ($C^{5'}$), 137.00 (OCH_2**C**), 147.45 ($C^{4a'}$), 148.75 ($C^{6'}$), 153.86 (C^8), 202.10 (C^6).

2,3:20,22-Bis-*O*-[2-(6-hydroxy-2,5,7,8-tetramethylchroman-2-yl)ethylidene]-20-hydroxyecdysone (IX). Hydrogen was passed through a suspension of 0.28 g (0.25 mmol) of compound **V** and 0.07 g of 10% Pd/C in 5 ml of anhydrous methanol until the reaction was complete (~3 h, TLC). The catalyst was filtered off, the filtrate was evaporated, and the residue was subjected to chromatography on silica gel (15 g) using chloroform as eluent. Yield 0.23 g (96%), mp 130–134°C, $[\alpha]_D^{20}$ = +24.5° (*c* = 1.82, CH_2Cl_2). ^{1}H NMR spectrum, δ, ppm: 0.71 s (3H, $C^{18}H_3$), 0.97 s (3H, $C^{19}H_3$), 1.15 s (3H, $C^{21}H_3$), 1.26 s (6H, $C^{26}H_3$, $C^{27}H_3$), 1.33 s (3H, 2′-CH_3), 1.34 s (3H, 2″-CH_3); 2.11 s, 2.16 s, and 2.18 s (6H each, CH_3); 2.62 s (4H, 4′-H, 4″-H), 3.59 m (1H, 22-H), 4.12 m (1H, 2-H), 4.46 m (1H, 3-H), 5.14 br.s (1H, 2‴-H), 5.21 br.s (1H, 2‴-H), 5.82 s (1H, 7-H). ^{13}C NMR spectrum, δ_C, ppm: 11.32, 11.85, and 12.26 (CH_3); 16.97 (C^{18}), 20.63 (C^{19}), 20.63 ($C^{4'}$, $C^{4''}$), 21.46 (C^{11}), 23.00 (C^{16}), 23.53 (C^{21}), 24.37 (2′-CH_3, 24.64 (2″-CH_3), 26.65 (C^{23}), 29.43 (C^{26}, C^{27}), 30.82 (C^{15}), 30.92 (C^4), 31.65 ($C^{3'}$), 31.95 ($C^{3''}$) 33.16 (C^{12}), 34.69 (C^9), 37.80 (C^1), 38.37 (C^{10}), 41.38 (C^{24}), 45.42 (C^{13}), 47.33 (C^5), 49.71 (C^{17}), 50.90 ($C^{1'''}$, $C^{1''''}$), 70.51 (C^{25}), 73.05 ($C^{2'}$), 73.32 ($C^{2''}$), 76.73 (C^3), 77.05 (C^2), 83.59 (C^{20}), 83.83 (C^{22}), 84.80 (C^{14}), 101.44 and 101.66 ($C^{2''''}$) 102.01 ($C^{2'''}$), 117.10 ($C^{8a'}$, $C^{8a''}$), 118.71 ($C^{5'}$, $C^{5''}$), 121.38 ($C^{8'}$, $C^{8''}$, C^7), 122.64 ($C^{7'}$, $C^{7''}$), 144.81 ($C^{4a'}$, $C^{4a''}$), 145.11 ($C^{6'}$), 163.21 (C^8), 203.01 (C^6). Mass spectrum: *m*/*z* 942.360 $[M + H]^+$. $C_{57}H_{80}O_{11}$. Calculated: *M* 941.248.

2,3-*O*-[2-(6-Hydroxy-2,5,7,8-tetramethylchroman-2-yl)ethylidene]-20,22-*O*-isopropylidene-20-hydroxyecdysone (X). Hydrogen was passed over a period of 3 h through a suspension of 0.12 g (0.14 mmol) of compound **VI** and 0.03 g of 10% Pd/C in 5 ml of anhydrous methanol. The catalyst was filtered off, the filtrate was evaporated, and the residue was subjected to column chromatography on silica gel (15 g) using chloroform as eluent. Yield 0.10 g (90%), mp 150–152°C, $[\alpha]_D^{20}$ = +10.44° (*c* = 3.76, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 0.80 s (3H, $C^{19}H_3$), 0.96 s (3H, $C^{18}H_3$), 1.17 s (3H, $C^{21}H_3$), 1.24 s (3H, $C^{26}H_3$), 1.25 s (3H, $C^{27}H_3$), 1.33 s [6H, $(CH_3)_2C$], 1.42 s (3H, 2′-CH_3), 2.10 s and 2.15 s (9H, CH_3), 2.62 m (2H, 4′-H), 3.67 m (1H, 22-H), 4.12 m (1H, 2-H), 4.41 m (1H, 3-H), 5.20 br.s (1H, 2‴-H), 5.83 s (1H, 7-H).

^{13}C NMR spectrum, δ_C, ppm: 11.31, 11.85, and 12.25 (CH_3); 17.04 (C^{18}), 20.56 (C^{19}), 20.57 ($C^{4'}$), 21.17 (C^{11}), 21.88 (C^{16}), 23.58 (C^{21}), 24.40 (C^{23}), 24.50 (2′-CH_3), 26.85 and 28.96 [(**C**H_3)$_2$C], 29.22 (C^{26}), 29.62 (C^{27}), 30.98 (C^{15}), 31.67 (C^4), 31.96 ($C^{3'}$), 34.76 (C^9), 34.77 (C^{12}), 37.77 (C^1), 38.34 (C^{10}), 41.38 (C^{24}), 45.42 (C^5), 47.47 (C^{13}), 49.02 (C^{17}), 50.79 ($C^{1'''}$), 70.39 (C^{25}), 73.29 ($C^{2'}$), 77.03 (C^2), 77.35 (C^3), 82.00 (C^{22}), 84.40 (C^{20}), 84.95 (C^{14}), 101.99 ($C^{2'''}$), 116.73 (C^{8a}), 118.69 ($C^{5''}$), 121.33 (C^7), 122.64 ($C^{7'}$), 122.99 ($C^{8'}$), 144.79 ($C^{4a''}$), 145.10 ($C^{6'}$), 163.44 (C^8), 202.82 (C^6). Found, %: C 71.50; H 9.00. $C_{45}H_{66}O_6$. Calculated, %: C 71.90; H 8.78.

This study was performed under financial support by the President of the Russian Federation (project no. NSh-6079.2008.3) and by the Academy of Sciences of Bashkortostan Republic.

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, vol. 33, no. 5, p. 655.
3. Lafont, R. and Dinan, L., *J. Insect Sci*., 2003, vol. 3, p. 1.
4. Bathori, M. and Pongracz, Z., *Cur. Med. Chem*., 2005, vol. 12, p. 153.
5. Odinokov, V.N., Galyautdinov, I.G., Nedopekin, D.V., and Khalilov, L.M., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2003, p. 220.
6. 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.