

## New Derivatives of 20-Hydroxyecdysone. Viticosterone E Synthesis

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**Abstract**—New 20,22-mono- and 2,3:20,22-diacetals of 20-hydroxyecdysone were synthesized, and some thereof were applied to the synthesis of 25-O-acetyl-20-hydroxyecdysone (viticosterone E).

Ecdysteroids that are by structure polyhydroxysteroids have been found in most classes of invertebrates, including insects, and have been isolated from numerous plant species. Their physiological role in insect organism consists in molting and metamorphosis control, they are involved in regulation of reproductive function and general physiologic processes, like metabolism [1]. The ecdysteroids functions in the plant life is not yet clear, but it is presumed that the compounds take part in protection from nonadapted insects (phitophages) [2]. Alongside free ecdysteroids there were also identified in natural objects their conjugates (derivatives at hydroxy groups) that as a rule belonged to minor components of ecdysteroid composition of plants and animals [3, 4]. The best known among them is 25-O-acetyl-20-hydroxyecdysone (viticosterone E), the minor component of ecdysteroids contained in a number of plant species [5–10]. Several preparation methods of viticosterone E were advanced based on acetylation of the tertiary 25-hydroxy group in the 20-hydroxyecdysone after protection of more reactive 2-, 3-, and 22-hydroxy groups by conversion into 2,3:20,22-diacetonide [6,11] or into 2,3-acetonide-20,22-phenylboronate [12]. However all methods afforded the target phitoeecdysteroid in a low yield, and viticosterone E proper was not sufficiently characterized.

The main problem in the synthesis of viticosterone E consists in selective deprotection of 20,22-hydroxy group leaving unaffected the 25-acetoxy group, whereas the hydrolysis of 2,3-acetonide protection is easily preformed. In order to choose the most adequate synthetic procedure for preparation of the target compound **XXVI** we prepared a series of 20-hydroxyecdysone (**I**) derivatives:

20,22-monoacetals **VII–XI**, and 2,3:20,22-diacetals **XII–XVI**.

In reaction of compound **I** with acetaldehyde (**II**) in the presence of phosphomolybdic acid (PMA) 20,22-O-ethylidene-20-hydroxyecdysone was formed as a mixture of 1'*R*- and 1'*S*-epimers (*RS*-**VII**) as evidenced by two pairs of signals from acetal carbons  $C^{1'}$  ( $\delta$  100.1 and 101.3 ppm) and  $C^{22}$  ( $\delta$  79.5 and 84.9 ppm) in the  $^{13}C$  NMR spectrum, and 2 quartet signals of protons attached thereto ( $\delta$  5.06 and 5.15 ppm,  $^3J$  5.0 Hz) in the  $^1H$  NMR spectrum (solvent  $C_5D_5N$ ). The modified procedure (keeping of cooled dispersion of compound **I** in acetaldehyde till complete dissolution followed by PMA addition) afforded configurationally uniform 2,3:20,22-bis acetal **XII** as proved by two separate signals of 20,22- and 2,3-acetal groups in the  $^{13}C$  NMR spectrum ( $\delta$  101.0 and 101.4 ppm for  $C^{1'}$  and  $C^{1''}$  respectively) and by the presence of only two quartets ( $^3J$  5 Hz) of protons linked to  $C^{1'}$  and  $C^{1''}$  in the  $^1H$  NMR spectrum (solvent  $CDCl_3$ ) ( $\delta$  5.04 and 5.09 ppm respectively). The very small quartet signals appearing at  $\delta$  ~5.25 and 5.36 ppm indicate that the probable diastereomers at the chiral centers  $C^{1'}$  and  $C^{1''}$  constitute an impurity not exceeding 5–10%. By hydrolysis of bisacetal **XII** we obtained configurationally uniform 20,22-acetal (*R*-**VII**). Its  $^{13}C$  NMR spectrum contains a unique signal from  $C^{1'}$  atom at  $\delta$  101.1, and in the  $^1H$  NMR spectrum (solvent  $CDCl_3$ ) appears a quartet at  $\delta$  5.04 ppm ( $^3J$  5 Hz). A faintly visible quartet at  $\delta$  5.28 ppm reveals the presence of an impurity of another epimer not exceeding 5–10%. The 2D NOESY-experiment showed a weak NOE-effect from the proton at  $C^{1'}$  atom to protons at  $C^{18}$  carbon and total absence of

NOE-correlation with  $\text{H}_3\text{C}^{21}$ . This result permits a conclusion that the 20,22-acetal obtained has *R*-configuration at the  $\text{C}^1$  atom where the methyl group (more bulky than a hydrogen atom) is located at the less sterically hindered side of the dioxolane ring (as seen from the Dreiding molecular model).

The reaction of substance **I** with carbonyl compounds **III–VI** in the presence of PMA gave rise to mixtures of monoacetals **VIII–XI** and diacetals **XIII–XVI** that were separated by column chromatography. The formation of cyclic acetals at 2,3- and 20,22-hydroxy groups is reflected in their  $^{13}\text{C}$  NMR spectra by downfield shift of signals belonging to atoms  $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^{20}$ , and  $\text{C}^{22}$ , and also in appearance of signals from acetal carbons in the region  $\delta$  105–110 ppm (95–97 ppm for compounds **XI** and **XVI**). In the  $^{13}\text{C}$  NMR spectra of compounds **IX**, **X** and **XIV**, **XV** obtained from compound **I** and ketones **IV** and **V** the signals from 2,3-acetal atoms of compounds **XIV** and **XV** appear in double set evidencing the presence of diastereomers whereas the signals of 20,22-acetal atoms are unique indicating their configurational uniformity. The partial hydrolysis of bisacetals **XIV** and **XV** afforded the corresponding chirally uniform 20,22-monoacetals **IX** and **X** existing apparently in the *R*-configuration where the more bulky  $\text{R}^2$  groups were located at the less sterically hindered side of the dioxolane ring.

A more complicated situation is observed in the  $^{13}\text{C}$  NMR spectra of acetals **XI** and **XVI** prepared from furfural (**VI**) apparently originating not only from the presence of chiral atoms  $\text{C}^1$  and  $\text{C}^{1'}$  in 1,3-dioxolane rings but from different mutual orientation of furan and 1,3-dioxolane rings. Consequently on converting bisacetal **XVI** into 20,22-acetal **XI** the  $^{13}\text{C}$  NMR spectrum of the latter contains 2 signals of acetal carbon. In the spectrum of acetal **XI** a double set of signals is also observed for atoms  $\text{C}^{17}$ ,  $\text{C}^{20}$  and  $\text{C}^{22}$ .

It was reported [13], that in reaction of 20-hydroxyecdysone **I** with trifluoroacetic anhydride a mixture was obtained (~1:1) of shidasterone and 20,22-O-(1-hydroxy-2,2,2-trifluoromethylethylidene)-20-hydroxyecdysone **XVII** [a mixture (~1:1) of 1'*R*- and 1'*S*-epimers]. We found conditions for this reaction affording compound **XVII** in 85% yield. Its reaction with acetone (**III**) in the presence of PMA gave the corresponding 2,3-acetonide **XVIII**.

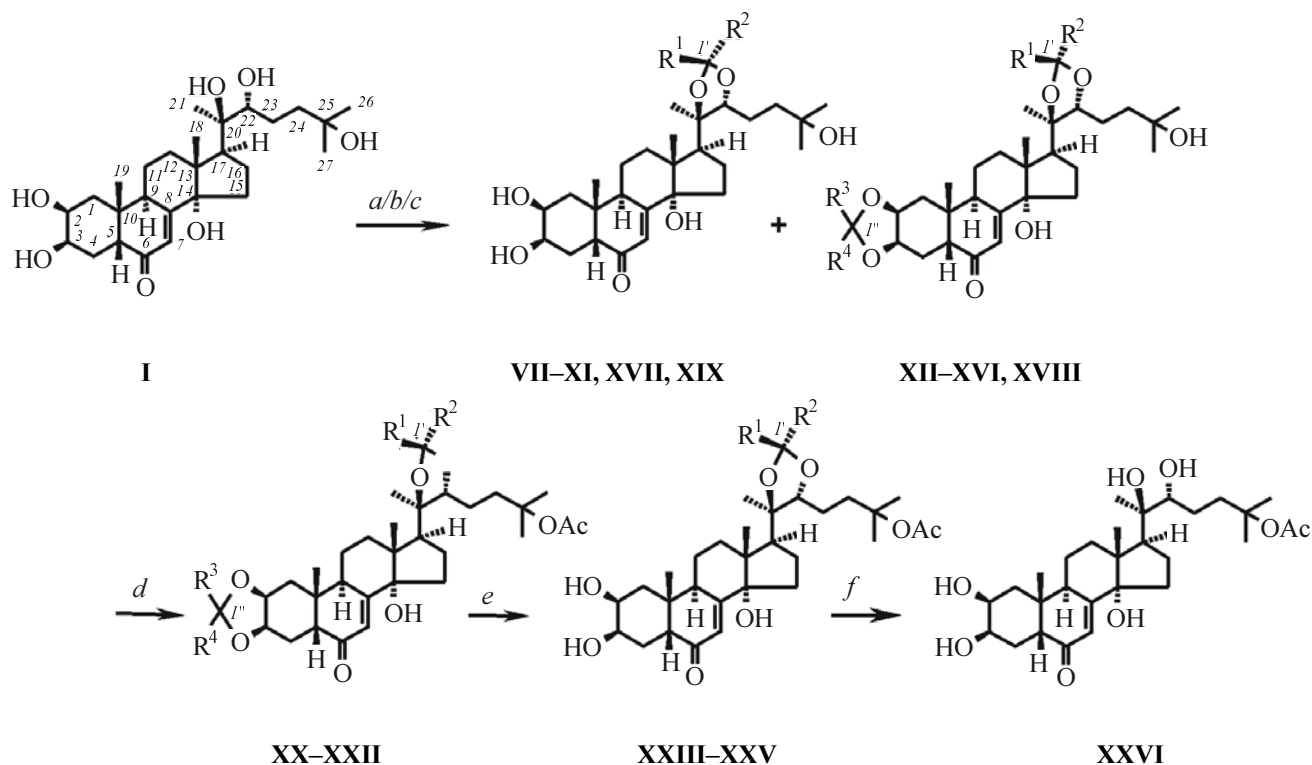
An unexpected result was obtained in reaction of 20-hydroxyecdysone **I** with 1,2-epoxyperfluorooctane that was known to isomerize into perfluorooctan-2-one [14]. Therefore we expected to prepare by this process the

corresponding polyfluorinated acetal of 20-hydroxyecdysone. However the reaction gave rise to 20,22-O-(4-hydroxybutylidene)-20-hydroxyecdysone (**XIX**). Its formation may be rationalized taking into account the possibility for epoxides to function as oxidants [15]. In our case tetrahydrofuran underwent oxidation into 2-hydroxy derivative capable of conversion into its tautomer, 4-hydroxybutanal that reacted with compound **I** to give acetal **XIX**. The structure of compound **XIX** was established from IR, UV,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The formation of 1,3-dioxolane ring is confirmed by the downfield shift of signals from  $\text{C}^{20}$  and  $\text{C}^{22}$  atoms in the  $^{13}\text{C}$  NMR spectrum ( $\Delta\delta$  7.5 and 7.2 ppm with respect to the corresponding signals in the spectrum of compound **I**) as is also observed in the spectra of 20,22-acetals **VII–XI**. A doublet signal of acetal atom  $\text{C}^1$  ( $\delta$  105.3 ppm) registered in the JMOD mode evidences that a hydrogen atom is linked thereto, and a triplet signal at  $\delta$  62.9 ppm belongs to  $\text{C}^4$  atom of a primary alcohol group. The single peak of the acetal  $\text{C}^1$  carbon testifies to the uniformity of its configuration that similarly to the structure of acetals **VII**, **IX–XI** is apparently *R*-configuration due to feasibility of the bulky substituent position on the more accessible side of the ring.

Inasmuch as the acid hydrolysis furnishing ecdysteroid **I** occurred cleanly both with acetals **VII–IX** and bisacetals **XII–XIV** further conversions into the target viticosterone **E** were carried out with bisacetals **XII–XIV**.

Prolonged storage of a mixture of an appropriate bisacetal **XII–XIV**, acetic anhydride, and pyridine in the presence of 4-(*N,N*-dimethylamino)pyridine (DMAP) resulted in formation of the corresponding 25-acetates **XX–XXII**. Therewith from the product of acetylation of the diastereomer mixture of bisacetal **XIV** we isolated alongside the target acetate **XXII** also a configurationally uniform bisacetal **XIV** as shown by single peaks of the acetal carbons of 2,3- ( $\delta$  110.4 ppm) and 20,22-dioxolane rings ( $\delta$  108.8 ppm). Apparently a partial deprotection from 2,3-acetal occurs by acidolysis in the less stable dioxolane ring where the more bulky ethyl group is located on the less sterically accessible *S*-*fac* side, and the bisacetal probably possesses *R*-configuration at both acetal atoms  $\text{C}^1$  and  $\text{C}^{1'}$ . The reduced specific rotation of the 1'*R*, 1''*R*-isomer **XIV** compared with the mixture of 1'*R*, 1''*R/S*-isomers **XIV** obviously shows that the specific rotation of 1'*R*, 1''*S*-isomer **XIV** is larger than that of the isolated epimer (1'*R*, 1''*R*-**XIV**).

The treatment with 70% AcOH of compounds **XX–XXII** cleanly converted them into the corresponding



*a*,  $R^1COR^2$  (**II–VI**)/PMA (for compounds **VII–XVI**); *b*, (1)  $(CF_3CO)_2O/CHCl_3$ ; (2)  $Me_2CO/PMA$  (for compound **XVIII**); – THF (for compound **XIX**); *d*,  $Ac_2O/Py$  – DMAP; *e*, 70% AcOH; *f*, 70% AcOH/ $ZnCl_2$ .  $R^1 = H$  (**II, VI, VII, XI, XII, XVI, XIX, XX, XXIII, XXIV**), Me (**III–V, VIII–X, XIII–XV, XXI, XXII, XXIV, XXV**), OH (**XVII, XVIII**);  $R^2 = Me$  (**II, III, VII, VIII, XII, XIII, XX, XXI, XXIII, XXIV**), Et (**IV, IX, XIV, XXII, XXV**),  $MeCOCH_2$  (**V, X, XV**), 2-furyl (**VI, XI, XVI**),  $CF_3$  (**XVII, XVIII**),  $HO(CH_2)_3$  (**XIX**);  $R^3 = H$  (**XII, XVI, XX, XXIII**), Me (**XIII–XV, XVIII, XXI, XXII, XXIV, XXV**);  $R^4 = Me$  (**XII, XIII, XVIII, XX, XXI, XXIII, XXIV**), Et (**XIV, XXII, XXV**),  $MeCOCH_2$  (**XV**), 2-furyl (**XVI**).

monoacetals **XXIII–XXV**, and hydrolysis of the latter ( $AcOH-ZnCl_2$ ) afforded the target phitoecdysteroid **XXVI**. The overall yield of viticosterone E (**XXVI**) calculated on diacetals **XII–XIV** amounted to 84, 35, and 32% respectively. Hence as the most feasible seems the synthesis of viticosterone E (**XXVI**) from diacetal **XII** along the route **XII**→**XX**→**XXIII**→**XXVI**.

#### EXPERIMENTAL

IR spectra of compounds were recorded on spectrometer Specord 75-IR (from pellets with KBr). UV spectra were taken on Specord M-40 instrument from solutions in EtOH.  $^1H$  and  $^{13}C$  NMR spectra were registered on spectrometer Bruker AM-300 (operating frequency for  $^1H$  300.13, for  $^{13}C$  75 MHz), solvents  $CDCl_3$ ,  $CD_3OD$ , or  $C_5D_5N$ . Chemical shifts are given in the  $\delta$  scale relative to TMS used as internal reference. Melting points were measured on a small Bëtius heating block. The specific rotation was determined on a polarimeter Perkin-Elmer-141. Control measurements by TLC were carried out on

Silufol plates, development with vanillin solution in ethanol acidified with sulfuric acid.

20-Hydroxyecdysone (**I**) was isolated from the plant species *Serratula coronata* [16]. Acetaldehyde (**II**) (Production certificate MPTU 6-09-5708-68), acetone (**III**), methyl ethyl ketone (**IV**) (Production certificate MPTU 6-09-3900-67), acetylacetone (**V**) (State standard GOST 10259-62), and furfural (**VI**) (State standard GOST 10930-64) were distilled before use. Phosphomolybdic acid (PMA) used had Production certificate TY 6-09-3540-78. Acetonides **VIII** and **XIII** were prepared from compounds **I** and **III** according to [17].

**20,22-O-[(1R)-Ethylidene]-20-hydroxyecdysone (R-VII)**. Stirring of 100 mg (0.19 mmol) of diacetal **XII** and 1 ml of 70% acetic acid at  $\sim 25^\circ C$  was continued till complete conversion of substrate ( $\sim 3$  h, TLC monitoring). The reaction mixture was diluted with water (3 ml), the reaction product was extracted with 1-butanol ( $3 \times 10$  ml), the combined extracts were washed with saturated NaCl solution, evaporated to dryness, and the residue was subjected to column chromatography (4 g of  $SiO_2$ , eluent

CHCl<sub>3</sub>–MeOH, 10:1), we obtained 92 mg (96%) of compound (*R*-**VII**), *R<sub>f</sub>* 0.3 (CHCl<sub>3</sub>–MeOH, 10:1), mp 118–119°C,  $[\alpha]_D^{25}$  29.8° (*C* 2.0, CHCl<sub>3</sub>). IR spectrum (KBr),  $\nu$ , cm<sup>-1</sup>: 3450, 1650. UV spectrum,  $\lambda_{\max}$ , nm: 242. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm (*J*, Hz): 0.81 s (3H, H<sub>3</sub>C<sup>18</sup>), 0.95 s (3H, H<sub>3</sub>C<sup>19</sup>), 1.12 s (3H, H<sub>3</sub>C<sup>21</sup>), 1.20 s (3H, H<sub>3</sub>C<sup>26</sup>), 1.29 s (3H, H<sub>3</sub>C<sup>27</sup>), 1.33 d (3H, CH<sub>3</sub>C<sup>1'</sup>, <sup>3</sup>*J* 5.0), 1.50–2.10 m (16H, CH<sub>2</sub>), 2.18 t (1H, HC<sup>17</sup>, <sup>3</sup>*J* 9.0), 2.39 t (1H, HC<sup>5</sup>, <sup>3</sup>*J* 9.0), 2.97 m (1H, HC<sup>9</sup>, *w*<sub>1/2</sub> 26), 3.58 m (1H, HC<sup>22</sup>, *w*<sub>1/2</sub> 18), 3.77 m (1H, HC<sup>2</sup>, *w*<sub>1/2</sub> 25), 4.01 m (1H, HC<sup>3</sup>, *w*<sub>1/2</sub> 12), 5.04 q and 5.28 q (1'*R*/1'*S* ~ 95:5) (1H, HC<sup>1'</sup>, <sup>3</sup>*J* 5.0), 5.82 d (1H, HC<sup>7</sup>, <sup>4</sup>*J* 2.0). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 17.0 q (C<sup>18</sup>), 18.9 t (C<sup>11</sup>), 21.4 t (C<sup>16</sup>), 21.6 q (CH<sub>3</sub>C<sup>1'</sup>), 22.9 q (C<sup>21</sup>), 23.2 t (C<sup>23</sup>), 24.0 q (C<sup>19</sup>), 28.0 t (C<sup>15</sup>), 30.8 q and 30.9 q (C<sup>26</sup> and C<sup>27</sup>), 31.8 t (C<sup>12</sup>), 33.8 t (C<sup>4</sup>), 34.8 d (C<sup>9</sup>), 36.6 t (C<sup>1</sup>), 38.1 s (C<sup>10</sup>), 41.2 t (C<sup>24</sup>), 47.2 s (C<sup>13</sup>), 49.7 d (C<sup>17</sup>), 50.0 d (C<sup>5</sup>), 67.4 d (C<sup>3</sup>), 67.7 d (C<sup>2</sup>), 70.7 s (C<sup>25</sup>), 83.7 s (C<sup>20</sup>), 84.4 d (C<sup>22</sup>), 84.9 s (C<sup>14</sup>), 101.1 d (C<sup>1'</sup>), 121.5 d (C<sup>7</sup>), 165.4 s (C<sup>8</sup>), 204.6 s (C<sup>6</sup>). Found, %: C 68.95; H 9.28. C<sub>29</sub>H<sub>46</sub>O<sub>7</sub>. Calculated, %: C 68.75; H 9.15.

**20,22-O-[(1*RS*)-Ethylidene]-20-hydroxyecdysone (*RS*-**VII**).** A suspension of 1.0 g (2.08 mmol) of compound **I**, 8.0 mg of PMA, and 125 ml of acetic aldehyde was stirred for 30 min at ~25°C. The reaction mixture was evaporated to 5 ml, 15 ml of 2% NaHCO<sub>3</sub> solution was added, and the reaction product was extracted into AcOEt (3×60 ml). The extract was evaporated in a vacuum, and the residue was subjected to chromatography on a column charged with 50 g of SiO<sub>2</sub> (eluent CHCl<sub>3</sub>–MeOH, 9:1). We obtained 0.95 g (90%) of compound (*RS*-**VII**) (*R/S* ~ 1:1), mp 98–102°C,  $[\alpha]_D^{22}$  32.1° (*C* 1.63, CHCl<sub>3</sub>). <sup>1</sup>H NMR spectrum (C<sub>5</sub>D<sub>5</sub>N),  $\delta$ , ppm (*J*, Hz): 0.92 s (3H, H<sub>3</sub>C<sup>18</sup>), 0.95 s (3H, H<sub>3</sub>C<sup>19</sup>), 1.26 s (3H, H<sub>3</sub>C<sup>21</sup>), 1.31 s (6H, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.38 d (3H, CH<sub>3</sub>C<sup>1'</sup>, <sup>3</sup>*J* 5.0), 1.50–2.20 m (16H, CH<sub>2</sub>), 2.3–2.5 m (1H, HC<sup>17</sup>), 2.68 t (1H, HC<sup>5</sup>, <sup>3</sup>*J* 8.0), 3.10 m (1H, HC<sup>9</sup>, *w*<sub>1/2</sub> 26), 3.77 m (1H, HC<sup>22</sup>, *w*<sub>1/2</sub> 18), 3.88 m (1H, HC<sup>3</sup>, *w*<sub>1/2</sub> 12), 4.10 m (1H, HC<sup>2</sup>, *w*<sub>1/2</sub> 25), 5.06 q and 5.15 q (1'*R*/1'*S* ~ 1:1) (1H, HC<sup>1'</sup>, <sup>3</sup>*J* 5.0), 6.10 br.s (1H, HC<sup>7</sup>, *w*<sub>1/2</sub> 6.5). <sup>13</sup>C NMR spectrum (C<sub>5</sub>D<sub>5</sub>N),  $\delta$ , ppm: 17.0 q (C<sup>18</sup>), 20.9 t (C<sup>11</sup>), 21.7 q and 21.9 q (CH<sub>3</sub>C<sup>1'</sup>), 22.0 t (C<sup>16</sup>), 23.6 q (C<sup>19</sup>), 24.0 t (C<sup>23</sup>), 24.2 q (C<sup>21</sup>), 26.2 t (C<sup>15</sup>), 29.5 q and 29.9 q (C<sup>26</sup> and C<sup>27</sup>), 31.3 t (C<sup>4</sup> and C<sup>12</sup>), 35.2 d (C<sup>9</sup>), 37.6 s (C<sup>10</sup>), 38.3 t (C<sup>1</sup>), 41.8 t (C<sup>24</sup>), 47.7 s (C<sup>13</sup>), 50.4 d (C<sup>17</sup>), 51.2 d (C<sup>5</sup>), 69.1 s (C<sup>25</sup>), 71.4 d (C<sup>3</sup>), 73.9 d (C<sup>2</sup>), 79.5 d and 84.9 d (C<sup>22</sup>), 84.2 s (C<sup>20</sup>), 84.6 s (C<sup>14</sup>), 101.1 d and 101.3 d (C<sup>1'</sup>), 121.0 d (C<sup>7</sup>), 164.8 s (C<sup>8</sup>), 202.1 s (C<sup>6</sup>).

**2,3:20,22-Bis-O-[(1*R*)-ethylidene]-20-hydroxyecdysone (**XII**).** A suspension of 1.0 g (2.08 mmol) of

compound **I** and 125 ml of acetic aldehyde was stirred at 2°C till complete dissolution of compound **I** (~72 h), then 4.0 mg of PMA was added, and the mixture was stirred at ~25°C for 10 min, 150 ml of water was added, and the product was extracted into AcOEt (3×200 ml). The extract was washed with water, evaporated in a vacuum, and the residue was subjected to column chromatography (100 g of SiO<sub>2</sub>, eluent CHCl<sub>3</sub>–MeOH, 30:1) to obtain 0.98 g (88%) of compound **XII**, *R<sub>f</sub>* 0.5 (CHCl<sub>3</sub>–MeOH, 10:1), mp 113–115°C,  $[\alpha]_D^{19}$  44.1° (*C* 3.23, CHCl<sub>3</sub>). IR spectrum (KBr),  $\nu$ , cm<sup>-1</sup>: 3450, 1720, 1655. UV spectrum,  $\lambda_{\max}$ , nm: 242. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm (*J*, Hz): 0.77 s (3H, H<sub>3</sub>C<sup>18</sup>), 0.93 s (3H, H<sub>3</sub>C<sup>19</sup>), 1.10 s (3H, H<sub>3</sub>C<sup>21</sup>), 1.19 s and 1.20 s (6H, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.33 d (3H, CH<sub>3</sub>C<sup>1'</sup>, <sup>3</sup>*J* 5.0), 1.38 d (3H, CH<sub>3</sub>C<sup>1'</sup>, <sup>3</sup>*J* 5.0), 1.46–2.47 m (18H, CH, CH<sub>2</sub>), 2.72 m (1H, HC<sup>9</sup>, *w*<sub>1/2</sub> 22), 3.57 m (1H, HC<sup>22</sup>, *w*<sub>1/2</sub> 14), 4.07 m (1H, HC<sup>3</sup>, *w*<sub>1/2</sub> 12), 4.15 m (1H, HC<sup>2</sup>, *w*<sub>1/2</sub> 30), 5.04 q (1H, HC<sup>1'</sup>, <sup>3</sup>*J* 5.0), 5.09 q (1H, HC<sup>1'</sup>, <sup>3</sup>*J* 5.0), 5.77 br.s (1H, HC<sup>7</sup>, *w*<sub>1/2</sub> 5). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 16.6 q (C<sup>18</sup>), 20.4 t (C<sup>11</sup>), 21.3 t (C<sup>16</sup>), 21.4 q and 21.5 q (CH<sub>3</sub>C<sup>1'</sup> and CH<sub>3</sub>C<sup>1''</sup>), 22.9 q (C<sup>21</sup>), 23.3 t (C<sup>23</sup>), 23.4 q (C<sup>19</sup>), 26.5 t (C<sup>15</sup>), 29.1 q and 29.5 q (C<sup>26</sup> and C<sup>27</sup>), 30.6 t (C<sup>12</sup>), 31.3 t (C<sup>4</sup>), 34.6 d (C<sup>9</sup>), 37.6 s (C<sup>10</sup>), 38.3 t (C<sup>1</sup>), 41.2 t (C<sup>24</sup>), 47.2 s (C<sup>13</sup>), 49.6 d (C<sup>17</sup>), 50.1 d (C<sup>5</sup>), 70.4 s (C<sup>25</sup>), 71.5 d (C<sup>3</sup>), 73.6 d (C<sup>2</sup>), 83.8 s (C<sup>20</sup>), 84.2 d (C<sup>22</sup>), 84.5 s (C<sup>14</sup>), 101.0 d (C<sup>1'</sup>), 101.4 d (C<sup>1''</sup>), 121.1 d (C<sup>7</sup>), 164.0 s (C<sup>8</sup>), 203.0 s (C<sup>6</sup>). Found, %: C 70.18; H 9.22. C<sub>31</sub>H<sub>48</sub>O<sub>7</sub>. Calculated, %: C 69.90; H 9.08.

**20,22-O-[(2*R*)-Butan-2-ylidene]-20-hydroxyecdysone (**IX**) and 2,3-O-(2*RS*-butan-2-ylidene)-20,22-O-[(2*R*)-butan-2-ylidene]-20-hydroxyecdysone (**XIV**).** A suspension of 1.0 g (2.08 mmol) of compound **I**, 4.0 mg of PMA, and 50 ml of methyl ethyl ketone (**IV**) was stirred for 5 min at ~25°C. The homogenization occurred within ~10 min, then the reaction mixture was concentrated and to the remaining 10 ml of solution 15 ml of 2% NaHCO<sub>3</sub> solution was added. The reaction products were extracted with AcOEt (3×60 ml). The extract was evaporated in a vacuum, and the residue was subjected to chromatography on a column charged with 50 g of SiO<sub>2</sub>, eluent CHCl<sub>3</sub>–MeOH, 9:1, to obtain 0.22 g (20%) of compound **IX**, *R<sub>f</sub>* 0.3 (CHCl<sub>3</sub>–MeOH, 9:1) and 0.95 g (78%) of compounds **XIV**, *R<sub>f</sub>* 0.5 (CHCl<sub>3</sub>–MeOH, 9:1).

**Compound (IX).** mp 120–121°C,  $[\alpha]_D^{15}$  41.2° (*C* 1.1, MeOH). IR spectrum (KBr),  $\nu$ , cm<sup>-1</sup>: 3400, 1655. UV spectrum,  $\lambda_{\max}$ , nm: 242. <sup>1</sup>H NMR spectrum (CD<sub>3</sub>OD),  $\delta$ , ppm (*J*, Hz): 0.82 s (3H, H<sub>3</sub>C<sup>18</sup>), 0.90–1.00 m (6H, H<sub>3</sub>C<sup>19</sup> and CH<sub>3</sub>CH<sub>2</sub>C<sup>1'</sup>), 1.15 s (3H, H<sub>3</sub>C<sup>21</sup>), 1.19 s and

1.20 s (6H, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.26 s (3H, CH<sub>3</sub>C<sup>I</sup>), 1.30–2.15 m (18H, CH<sub>2</sub>), 2.25–2.40 m (2H, HC<sup>5</sup> and HC<sup>17</sup>), 3.15 m (1H, HC<sup>9</sup>, *w*<sub>1/2</sub> 25), 3.70 m (1H, HC<sup>22</sup>, *w*<sub>1/2</sub> 17), 3.85 m (1H, HC<sup>2</sup>, *w*<sub>1/2</sub> 22), 3.96 m (1H, HC<sup>3</sup>, *w*<sub>1/2</sub> 12), 5.81 d (1H, HC<sup>7</sup>, <sup>3</sup>*J* 2.0). <sup>13</sup>C NMR spectrum (CD<sub>3</sub>OD), δ, ppm\*: 9.6 q (CH<sub>3</sub>CH<sub>2</sub>C<sup>I</sup>), 17.7 q (C<sup>18</sup>), 21.5 t (C<sup>11</sup>), 22.2 t (C<sup>16</sup>), 23.0 q (C<sup>21</sup>), 24.2 q (C<sup>19</sup>), 24.5 q (CH<sub>3</sub>C<sup>I</sup>), 24.7 t (C<sup>23</sup>), 29.1 q and 29.5 q (C<sup>26</sup> and C<sup>27</sup>), 31.7 t (C<sup>15</sup>), 32.3 t (C<sup>12</sup>), 32.8 t (C<sup>4</sup>), 35.1 d (C<sup>9</sup>), 36.1 t (CH<sub>2</sub>C<sup>I</sup>), 37.4 t (C<sup>I</sup>), 39.2 s (C<sup>10</sup>), 42.2 t (C<sup>24</sup>), 50.6 d (C<sup>17</sup>), 51.7 d (C<sup>5</sup>), 68.5 d (C<sup>3</sup>), 68.6 d (C<sup>2</sup>), 71.1 s (C<sup>25</sup>), 83.0 d (C<sup>22</sup>), 85.3 s (C<sup>14</sup>), 85.4 s (C<sup>20</sup>), 109.9 s (C<sup>I</sup>), 122.1 d (C<sup>7</sup>), 167.6 s (C<sup>8</sup>), 206.4 s (C<sup>6</sup>). Found, %: C 69.84; H 9.60. C<sub>31</sub>H<sub>50</sub>O<sub>7</sub>. Calculated, %: C 69.63; H 9.42.

**Compound (XIV).** mp 128–131°C, [α]<sub>D</sub><sup>25</sup> 35.0° (C 3.8, CHCl<sub>3</sub>). IR spectrum (KBr), ν, cm<sup>-1</sup>: 3400, 1655. UV spectrum, λ<sub>max</sub>, nm: 242. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm (*J*, Hz): 0.77 s (3H, H<sub>3</sub>C<sup>18</sup>), 0.89–0.91 m (9H, H<sub>3</sub>C<sup>19</sup>, CH<sub>3</sub>CH<sub>2</sub>C<sup>I</sup> and CH<sub>3</sub>CH<sub>2</sub>C<sup>II</sup>), 1.12 s (3H, H<sub>3</sub>C<sup>21</sup>), 1.20 s and 1.21 s (6H, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.25 s (3H, CH<sub>3</sub>C<sup>I</sup>), 1.40 s (3H, CH<sub>3</sub>C<sup>II</sup>), 1.45–1.85 m (20H, CH<sub>2</sub>), 2.10–2.40 m (2H, HC<sup>5</sup> and HC<sup>17</sup>), 2.77 m (1H, HC<sup>9</sup>, *w*<sub>1/2</sub> 35), 3.62 m (1H, HC<sup>22</sup>, *w*<sub>1/2</sub> 15), 4.14–4.25 m (2H, HC<sup>2</sup> and HC<sup>3</sup>), 5.73 d (1H, HC<sup>7</sup>, <sup>4</sup>*J* 2.0). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 8.9 q and 9.0 q (CH<sub>3</sub>CH<sub>2</sub>C<sup>I</sup> and CH<sub>3</sub>CH<sub>2</sub>C<sup>II</sup>), 16.9 q (C<sup>18</sup>), 20.4 t (C<sup>11</sup>), 21.1 t (C<sup>16</sup>), 22.1 q (C<sup>21</sup>), 23.5 q and 23.6 q (CH<sub>3</sub>C<sup>I</sup> and CH<sub>3</sub>C<sup>II</sup>), 25.2 q (C<sup>19</sup>), 26.6 t (C<sup>23</sup>), 28.9 q and 29.7 q (C<sup>26</sup> and C<sup>27</sup>), 30.9 t (C<sup>15</sup>), 31.4 t (C<sup>12</sup>), 32.3 t (C<sup>4</sup>), 34.4 d (C<sup>9</sup>), 34.9 t and 35.6 t (C<sup>I</sup>), 37.6 t (MeCH<sub>2</sub>C<sup>I</sup> and MeCH<sub>2</sub>C<sup>II</sup>), 37.7 s (C<sup>10</sup>), 41.3 t (C<sup>24</sup>), 47.4 s (C<sup>13</sup>), 49.1 d (C<sup>17</sup>), 50.6 d and 50.7 d (C<sup>5</sup>), 70.2 C (C<sup>25</sup>), 71.1 d, 71.6 d and 72.0 d (C<sup>2</sup> and C<sup>3</sup>), 81.6 d (C<sup>22</sup>), 84.0 s (C<sup>20</sup>), 84.7 s (C<sup>14</sup>), 108.8 s (C<sup>I</sup>), 110.1 s and 110.4 s (C<sup>II</sup>), 121.2 d (C<sup>7</sup>), 163.6 s (C<sup>8</sup>), 202.9 s (C<sup>6</sup>). Found, %: C 71.66; H 9.71. C<sub>35</sub>H<sub>56</sub>O<sub>7</sub>. Calculated, %: C 71.39; H 9.59.

**20,22-O-[(1*R*)-4-Oxopentan-2-ylidene]-20-hydroxyecdysone (X)** and **2,3-O-[(2*RS*)-4-oxopentan-2-ylidene]-20,22-O-[(1*R*)-4-oxopentan-2-ylidene]-20-hydroxyecdysone (XV).** A suspension of 1.0 g (2.08 mmol) of compound **I**, 4.0 mg of PMA, and 10 ml of acetylacetone **V** was stirred at ~25°C till homogenization of the reaction mixture (~50 min) that was then charged on a column with 100 g of SiO<sub>2</sub> and washed with CHCl<sub>3</sub> to complete removal of acetylacetone. Then elution was performed with a mixture

\* The signal of C<sup>13</sup> atom in the <sup>13</sup>C NMR spectrum of compound **IX** is overlapped with the multiplet of the solvent (δ 49 ppm).

CHCl<sub>3</sub>–MeOH, 20:1. We obtained 0.47 g (40%) of compound **X**, *R<sub>f</sub>* 0.4 (CHCl<sub>3</sub>–MeOH, 7:1), and 0.80 g (60%) of compound **XV**, *R<sub>f</sub>* 0.6 (CHCl<sub>3</sub>–MeOH, 7:1).

**Compound (X).** mp 148–150°C, [α]<sub>D</sub><sup>15</sup> 32.1° (C 2.1, MeOH). IR spectrum (KBr), cm<sup>-1</sup>: 3400, 1655. UV spectrum, λ<sub>max</sub>, nm: 242. <sup>1</sup>H NMR spectrum (C<sub>5</sub>D<sub>5</sub>N), δ, ppm (*J*, Hz): 0.90 s (3H, H<sub>3</sub>C<sup>18</sup>), 1.05 s (3H, H<sub>3</sub>C<sup>19</sup>), 1.35 s (9H, H<sub>3</sub>C<sup>21</sup>, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.54 s (3H, CH<sub>3</sub>C<sup>I</sup>), 2.33 s (3H, CH<sub>3</sub>CO), 1.60–2.50 m (18H, CH<sub>2</sub>), 2.73 m (1H, HC<sup>17</sup>, *w*<sub>1/2</sub> 17), 3.00 m (1H, HC<sup>5</sup>, *w*<sub>1/2</sub> 25), 3.57 m (1H, HC<sup>9</sup>, *w*<sub>1/2</sub> 29), 3.93 d.d (1H, HC<sup>22</sup>, <sup>3</sup>*J* 9.0 and 2.0), 4.15–4.25 m (2H, HC<sup>2</sup> and HC<sup>3</sup>), 6.23 br.s (1H, HC<sup>7</sup>, *w*<sub>1/2</sub> 10). <sup>13</sup>C NMR spectrum (C<sub>5</sub>D<sub>5</sub>N), δ, ppm: 17.0 q (C<sup>18</sup>), 20.7 t (C<sup>11</sup>), 21.8 t (C<sup>16</sup>), 22.0 q (C<sup>21</sup>), 23.9 t (C<sup>23</sup>), 24.2 q (C<sup>19</sup>), 25.2 q (CH<sub>3</sub>C<sup>I</sup>), 29.5 q and 29.7 q (C<sup>26</sup> and C<sup>27</sup>), 31.3 t (C<sup>15</sup>), 31.4 t (C<sup>12</sup>), 31.6 q (CH<sub>3</sub>CO), 32.2 t (C<sup>4</sup>), 34.1 d (C<sup>9</sup>), 37.6 t (C<sup>I</sup>), 38.4 s (C<sup>10</sup>), 41.6 t (C<sup>24</sup>), 47.5 s (C<sup>13</sup>), 49.6 d (C<sup>17</sup>), 51.1 d (C<sup>5</sup>), 56.4 t (CH<sub>2</sub>CO), 67.8 d (C<sup>3</sup>), 67.9 d (C<sup>2</sup>), 69.0 s (C<sup>25</sup>), 82.0 d (C<sup>22</sup>), 83.8 s (C<sup>14</sup>), 85.3 s (C<sup>20</sup>), 106.0 s (C<sup>I</sup>), 121.5 d (C<sup>7</sup>), 165.3 s (C<sup>8</sup>), 203.4 s (C<sup>6</sup>), 205.8 s (MeCO). Found, %: C 68.53; H 9.00. C<sub>32</sub>H<sub>50</sub>O<sub>8</sub>. Calculated, %: C 68.30; H 8.96.

**Compound (XV).** mp 153–155°C, [α]<sub>D</sub><sup>15</sup> 18.8° (C 1.7, CHCl<sub>3</sub>). IR spectrum (KBr), ν, cm<sup>-1</sup>: 3400, 1655. UV spectrum, λ<sub>max</sub>, nm: 243. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm (*J*, Hz): 0.76 s (3H, H<sub>3</sub>C<sup>18</sup>), 0.94 s (3H, H<sub>3</sub>C<sup>19</sup>), 1.19 s and 1.20 s (9H, H<sub>3</sub>C<sup>21</sup>, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.32 s (3H, CH<sub>3</sub>C<sup>II</sup>), 1.48 s (3H, CH<sub>3</sub>C<sup>I</sup>), 2.15 s and 2.18 s (6H, CH<sub>3</sub>CO), 1.40–2.40 m (20H, CH<sub>2</sub>), 2.65–2.82 m (3H, HC<sup>5</sup>, HC<sup>9</sup> and HC<sup>17</sup>), 3.63 m (1H, HC<sup>22</sup>, *w*<sub>1/2</sub> 17), 4.25 m (2H, HC<sup>2</sup> and HC<sup>3</sup>, *w*<sub>1/2</sub> 9), 5.77 br.s (1H, HC<sup>7</sup>, *w*<sub>1/2</sub> 5). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 17.0 q (C<sup>18</sup>), 20.4 t (C<sup>11</sup>), 21.1 t (C<sup>16</sup>), 23.2 t (C<sup>23</sup>), 23.4 q (C<sup>21</sup>), 24.5 q (C<sup>19</sup>), 25.0 q (CH<sub>3</sub>C<sup>I</sup>), 26.2 t (C<sup>4</sup>), 26.9 q (CH<sub>3</sub>C<sup>II</sup>), 29.2 q and 29.4 q (C<sup>26</sup> and C<sup>27</sup>), 30.8 t (C<sup>15</sup>), 31.2 t (C<sup>12</sup>), 31.6 q and 31.8 q (CH<sub>3</sub>COCH<sub>2</sub>C<sup>I</sup> and CH<sub>3</sub>COCH<sub>2</sub>C<sup>II</sup>), 34.2 d and 34.3 d (C<sup>9</sup>), 37.4 t (C<sup>I</sup>), 37.6 s and 37.7 s (C<sup>10</sup>), 41.0 t (C<sup>24</sup>), 47.3 s and 47.4 s (C<sup>13</sup>), 48.8 d (C<sup>17</sup>), 50.5 d and 50.8 d (C<sup>5</sup>), 53.2 t and 55.3 t (OCCH<sub>2</sub>C<sup>II</sup>), 56.3 t (OCCH<sub>2</sub>C<sup>I</sup>), 70.3 s (C<sup>25</sup>), 71.3 d, 71.9 d, 72.0 d and 72.3 d (C<sup>2</sup> and C<sup>3</sup>), 81.6 d (C<sup>22</sup>), 84.4 s (C<sup>14</sup>), 84.9 s (C<sup>20</sup>), 105.9 s (C<sup>I</sup>), 107.0 s and 107.2 s (C<sup>II</sup>), 121.1 d (C<sup>7</sup>), 163.4 s (C<sup>8</sup>), 202.6 s (C<sup>6</sup>), 205.8 s and 206.1 s (OCC<sup>II</sup>), 206.5 s (OCC<sup>I</sup>). Found, %: C 69.10; H 8.89. C<sub>37</sub>H<sub>56</sub>O<sub>9</sub>. Calculated, %: C 68.92; H 8.75.

**20,22-O-[(1*R*)-Furfurylidene]-20-hydroxyecdysone (XI)** and **2,3-O-[(1*RS*)-furfurylidene]-20,22-O-[(1*R*)-furfurylidene]-20-hydroxyecdysone (XVI).** A suspension of 1.0 g (2.08 mmol) of compound **I**, 4.0 mg

of PMA. and 30 ml furfural (**VI**) was stirred at  $\sim 25^\circ\text{C}$  till the reaction mixture became completely homogeneous ( $\sim 24$  h), then it was evaporated to 10 ml, 15 ml of 2%  $\text{NaHCO}_3$  solution was added, and reaction products were extracted into  $\text{AcOEt}$  ( $3 \times 60$  ml). The extract was evaporated to dryness, and the residue was subjected to chromatography on a column charged with 100 g of  $\text{SiO}_2$ , eluent  $\text{CHCl}_3$ – $\text{MeOH}$ , 25:1. We obtained 0.29 g (25%) of compound **XI**,  $R_f$  0.4 ( $\text{CHCl}_3$ – $\text{MeOH}$ , 7:1) and 0.93 g (70%) of compound **XVI**,  $R_f$  0.6 ( $\text{CHCl}_3$ – $\text{MeOH}$ , 7:1).

**Compound (XI)**. mp  $131$ – $134^\circ\text{C}$ ,  $[\alpha]_D^{22}$   $49.4^\circ$  ( $C$  1.7,  $\text{CH}_3\text{OH}$ ).  $^1\text{H}$  NMR spectrum ( $\text{C}_5\text{D}_5\text{N}$ ),  $\delta$ , ppm ( $J$ , Hz): 0.96 s (6H,  $\text{H}_3\text{C}^{18}$  and  $\text{H}_3\text{C}^{19}$ ), 1.34 s (6H,  $\text{H}_3\text{C}^{26}$  and  $\text{H}_3\text{C}^{27}$ ), 1.43 s (3H,  $\text{H}_3\text{C}^{21}$ ), 1.30–2.20 m (16H,  $\text{CH}_2$ ), 2.35–2.55 m (1H,  $\text{HC}^{17}$ ), 2.80–3.00 m (1H,  $\text{HC}^5$ ), 3.52 m (1H,  $\text{HC}^9$ ,  $w_{1/2}$  26), 3.98 m (1H,  $\text{HC}^{22}$ ,  $w_{1/2}$  19), 4.12–4.26 m (2H,  $\text{HC}^2$  and  $\text{HC}^3$ ), 6.10 s and 6.26 s (1H,  $\text{HC}''$ ), 6.17–6.21 m [1H,  $\text{HC}^4(\text{furyl})$ ], 6.42 br.s (1H,  $\text{HC}^7$ ,  $w_{1/2}$  6), 6.60–6.70 m [1H,  $\text{HC}^3(\text{furyl})$ ], 7.57–7.68 m [1H,  $\text{HC}^5(\text{furyl})$ ].  $^{13}\text{C}$  NMR spectrum ( $\text{C}_5\text{D}_5\text{N}$ ),  $\delta$ , ppm: 16.9 q and 17.0 q ( $\text{C}^{18}$ ), 20.6 t and 21.1 t ( $\text{C}^{11}$ ), 22.0 t ( $\text{C}^{16}$ ), 18.9 q and 22.1 q ( $\text{C}^{21}$ ), 24.0 q ( $\text{C}^{19}$ ), 23.9 t and 24.4 t ( $\text{C}^{23}$ ), 29.7 t ( $\text{C}^{15}$ ), 29.4 q and 29.7 q ( $\text{C}^{26}$  and  $\text{C}^{27}$ ), 31.2 t and 31.3 t ( $\text{C}^{12}$ ), 32.1 t ( $\text{C}^4$ ), 34.0 d ( $\text{C}^9$ ), 37.5 t ( $\text{C}^1$ ), 38.3 s ( $\text{C}^{10}$ ), 41.6 t and 41.7 t ( $\text{C}^{24}$ ), 47.3 s and 47.4 s ( $\text{C}^{13}$ ), 49.6 d, 50.3 d and 51.0 d ( $\text{C}^5$  and  $\text{C}^{17}$ ), 67.7 d and 67.8 d ( $\text{C}^2$  and  $\text{C}^3$ ), 69.0 s ( $\text{C}^{25}$ ), 82.9 d and 84.8 d ( $\text{C}^{22}$ ), 83.8 s and 85.7 s ( $\text{C}^{20}$ ), 84.9 s ( $\text{C}^{14}$ ), 95.7 d and 97.3 d ( $\text{C}^7$ ), 108.4 d, 109.3 d and 110.5 d [ $\text{C}^3(\text{furyl})$ ,  $\text{C}^4(\text{furyl})$  and  $\text{C}^5(\text{furyl})$ ], 121.5 d ( $\text{C}^7$ ), 152.4 s and 153.8 s [ $\text{C}^2(\text{furyl})$ ], 165.2 s ( $\text{C}^8$ ), 203.4 s ( $\text{C}^6$ ). Found, %: C 69.99; H 8.45.  $\text{C}_{32}\text{H}_{46}\text{O}_8$ . Calculated, %: C 68.79; H 8.30.

**Compound (XVI)**. mp  $138$ – $140^\circ\text{C}$ ,  $[\alpha]_D^{22}$   $42.4^\circ$  ( $C$  2.1,  $\text{CH}_3\text{OH}$ ).  $^1\text{H}$  NMR spectrum ( $\text{C}_5\text{D}_5\text{N}$ ),  $\delta$ , ppm ( $J$ , Hz): 0.98 s (6H,  $\text{H}_3\text{C}^{18}$  and  $\text{H}_3\text{C}^{19}$ ), 1.32 s (6H,  $\text{H}_3\text{C}^{26}$  and  $\text{H}_3\text{C}^{27}$ ), 1.50 s (3H,  $\text{H}_3\text{C}^{21}$ ), 1.65–2.55 m (16H,  $\text{CH}_2$ ), 2.55–2.65 m (1H,  $\text{HC}^{17}$ ), 2.83 m (1H,  $\text{HC}^5$ ,  $w_{1/2}$  28), 3.19 m (1H,  $\text{HC}^9$ ,  $w_{1/2}$  25), 3.99 m (1H,  $\text{HC}^{22}$ ,  $w_{1/2}$  15), 4.06–4.27 m (1H,  $\text{HC}^2$ ), 4.34–4.52 m (1H,  $\text{HC}^3$ ), 6.01 s and 6.32 s (1H,  $\text{HC}''$ ), 6.11 s and 6.27 s (1H,  $\text{HC}^7$ ), 6.12–6.17 m [2H,  $2\text{HC}^4(\text{furyl})$ ], 6.40 br.s (1H,  $\text{HC}^7$ ,  $w_{1/2}$  16), 6.54–6.71 m [2H,  $2\text{HC}^3(\text{furyl})$ ], 7.57–7.66 m [2H,  $2\text{HC}^5(\text{furyl})$ ].  $^{13}\text{C}$  NMR spectrum ( $\text{C}_5\text{D}_5\text{N}$ ),  $\delta$ , ppm: 17.0 q and 17.1 q ( $\text{C}^{18}$ ), 19.0 q and 22.5 q ( $\text{C}^{21}$ ), 20.8 t and 21.2 t ( $\text{C}^{11}$ ), 20.6 t and 22.1 t ( $\text{C}^{16}$ ), 23.3 q and 23.5 q ( $\text{C}^{19}$ ), 24.0 t and 24.5 t ( $\text{C}^{23}$ ), 26.4 t ( $\text{C}^{15}$ ), 29.5 q and 29.8 q ( $\text{C}^{26}$  and  $\text{C}^{27}$ ), 31.2 t and 31.3 t ( $\text{C}^{12}$ ), 35.1 t and 37.4 t ( $\text{C}^4$ ), 34.6 d and 35.2 d ( $\text{C}^9$ ), 37.3 t ( $\text{C}^1$ ), 37.7 s ( $\text{C}^{10}$ ), 41.7 t and 41.8 t ( $\text{C}^{24}$ ), 47.7 s and 47.8 s ( $\text{C}^{13}$ ), 49.7 d, 50.4 d and 51.0 d ( $\text{C}^5$  and  $\text{C}^{17}$ ), 69.1 s ( $\text{C}^{25}$ ), 72.2 d,

72.4 d, 72.9 d and 74.3 d ( $\text{C}^2$  and  $\text{C}^3$ ), 83.0 d and 84.9 d ( $\text{C}^{22}$ ), 83.8 s and 85.8 s ( $\text{C}^{20}$ ), 85.0 s ( $\text{C}^{14}$ ), 95.8 d and 96.3 d ( $\text{C}^{11}$ ), 97.4 d ( $\text{C}^7$ ), 108.4 d, 108.6 d, 109.3 d, 109.7 d, 110.5 d and 110.6 d [ $2\text{C}^3(\text{furyl})$ ,  $2\text{C}^4(\text{furyl})$  and  $2\text{C}^5(\text{furyl})$ ], 121.0 d ( $\text{C}^7$ ), 151.8 s, 152.5 s, 153.3 s and 153.9 s [ $2\text{C}^2(\text{furyl})$ ], 164.6 s and 164.8 s ( $\text{C}^8$ ), 201.8 s and 202.0 s ( $\text{C}^6$ ). Found, %: C 70.01; H 7.74.  $\text{C}_{37}\text{H}_{48}\text{O}_9$ . Calculated, %: C 69.79; H 7.60.

**2,3-O-Isopropylidene-20,22-O-[(1RS)-1-hydroxy-2,2,2-trifluoroethylidene]-20-hydroxyecdysone or (20R,22R)-2,3-O-isopropylidene-20,22-O-[(1RS)-1-hydroxy-2,2,2-trifluoroethylidene]-2 $\beta$ ,3 $\beta$ ,14 $\alpha$ ,25-tetrahydroxy-5 $\beta$ -cholest-7-en-6-one (XVIII)**. Stirring of 0.5 g (1.04 mmol) of compound **I**, 0.65 g (3.10 mmol) of trifluoroacetic anhydride, and 5 ml of chloroform at  $\sim 25^\circ\text{C}$  till formation of a homogeneous solution continued  $\sim 15$  min and then was carried on till complete conversion of the initial compound **I** ( $\sim 24$  h, TLC monitoring, eluent  $\text{CHCl}_3$ – $\text{MeOH}$ , 5:1). The reaction mixture was evaporated to dryness, and the residue was subjected to column chromatography (20 g of  $\text{SiO}_2$ , eluent  $\text{CHCl}_3$ – $\text{MeOH}$ , 6:1) to obtain 0.51 g (85%) of compound **XVII**,  $R_f$  0.3 ( $\text{CHCl}_3$ – $\text{MeOH}$ , 6:1), mp  $139$ – $140.5^\circ\text{C}$ ,  $[\alpha]_D^{24}$   $38.9^\circ$  ( $C$  1.44,  $\text{CHCl}_3$ ), IR, UV,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were identical to those published before [13]. The reaction product was placed into 50 ml of acetone, 20.0 mg of PMA was added to the dispersion, and it was stirred for 15 min at  $\sim 25^\circ\text{C}$ . The reaction mixture was subjected to chromatography on a column charged with 50 g of  $\text{SiO}_2$  (eluent  $\text{CHCl}_3$ – $\text{MeOH}$ , 6:1) to obtain 24 mg (25%) of compound **XVII**,  $R_f$  0.3 ( $\text{CHCl}_3$ – $\text{MeOH}$ , 6:1) and 0.35 g (70%) of compound **XVIII**,  $R_f$  0.4 ( $\text{CHCl}_3$ – $\text{MeOH}$ , 6:1).

**Compound (XVIII)**. mp  $131$ – $133^\circ\text{C}$ ,  $[\alpha]_D^{24}$   $31.2^\circ$  ( $C$  1.44,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR spectrum ( $\text{C}_5\text{D}_5\text{N}$ ),  $\delta$ , ppm ( $J$ , Hz): 0.87 s and 0.92 s (3H,  $\text{H}_3\text{C}^{18}$ ), 0.96 s (3H,  $\text{H}_3\text{C}^{19}$ ), 1.23 s and 1.42 s (3H,  $\text{H}_3\text{C}^{21}$ ), 1.28 s and 1.33 s (6H,  $\text{H}_3\text{C}^{26}$  and  $\text{H}_3\text{C}^{27}$ ), 1.53 s (6H,  $\text{CH}_3\text{CCH}_3$ ), 1.80–2.45 m (16H,  $\text{CH}_2$ ), 2.48–2.58 m (1H,  $\text{HC}^{17}$ ), 2.80 m (1H,  $\text{HC}^5$ ,  $w_{1/2}$  30), 3.15 m (1H,  $\text{HC}^9$ ,  $w_{1/2}$  25), 4.10 m (1H,  $\text{HC}^3$ ,  $w_{1/2}$  13), 4.15 m (1H,  $\text{HC}^2$ ,  $w_{1/2}$  23), 4.45 d.d (1H,  $\text{HC}^{22}$ ,  $^3J$  10 and 3), 6.15 m (1H,  $\text{HC}^7$ ,  $w_{1/2}$  7).  $^{13}\text{C}$  NMR spectrum ( $\text{C}_5\text{D}_5\text{N}$ ),  $\delta$ , ppm: 17.2 q and 17.4 q ( $\text{C}^{21}$ ), 18.0 q ( $\text{C}^{18}$ ), 21.4 t and 21.5 t ( $\text{C}^{11}$ ), 22.1 t and 22.3 t ( $\text{C}^{16}$ ), 23.8 q ( $\text{C}^{19}$ ), 26.8 q and 27.3 q ( $\text{Me}_2\text{C}$ ), 27.0 t ( $\text{C}^{23}$ ), 28.9 q and 29.5 q ( $\text{C}^{26}$  and  $\text{C}^{27}$ ), 31.5 t and 31.6 t ( $\text{C}^{15}$ ), 31.7 t ( $\text{C}^4$ ), 32.0 t ( $\text{C}^{12}$ ), 35.0 d and 35.1 d ( $\text{C}^9$ ), 38.0 s ( $\text{C}^{10}$ ), 38.1 t ( $\text{C}^1$ ), 41.7 t ( $\text{C}^{24}$ ), 48.0 s and 48.2 s ( $\text{C}^{13}$ ), 50.1 d and 50.2 d ( $\text{C}^{17}$ ), 51.6 d ( $\text{C}^5$ ), 69.0 C and 69.4 s ( $\text{C}^{25}$ ), 72.1 d and 72.5 d ( $\text{C}^2$  and  $\text{C}^3$ ), 84.0 d and 86.8 d

(C<sup>22</sup>), 84.1 s and 84.2 s (C<sup>14</sup>), 87.2 s and 89.6 s (C<sup>20</sup>), 108.2 s (CMe<sub>2</sub>), 112.6 q (<sup>2</sup>J<sub>CF</sub> 34.5) and 113.3 q (CCF<sub>3</sub>, <sup>2</sup>J<sub>CF</sub> 35.1), 121.3 d (C<sup>7</sup>), 122.1 q (<sup>1</sup>J<sub>CF</sub> 283) and 122.7 q (CF<sub>3</sub>, <sup>1</sup>J<sub>CF</sub> 289), 164.6 s (C<sup>8</sup>), 202.3 s (C<sup>6</sup>). Found, %: C 62.45; H 7.80. C<sub>32</sub>H<sub>47</sub>O<sub>8</sub>F<sub>3</sub>. Calculated, %: C 62.32; H 7.68.

**20,22-O-[(1R)-4-Hydroxybutylidene]-20-hydroxy-ecdysone, or (20R,22R)-20,22-O-[(1R)-4-hydroxy-butylidene]-2β,3β,14α,25-tetrahydroxy-5β-cholest-7-en-6-one (XIX).** To a suspension of 0.50 g (1.04 mmol) of compound **I** in a mixture of 5 ml of THF and 5 ml of CHCl<sub>3</sub> at ~25°C was added while stirring 0.83 g (2.00 mmol) of 1,2-epoxyperfluorooctane,\* in 1 min the reaction mixture turned homogeneous, and the stirring continued for another 2 h. Then the reaction mixture was applied to a column charged with 30 g of SiO<sub>2</sub>, and the nonpolar compounds were eluted with chloroform (~100 ml). Subsequent elution with a mixture CHCl<sub>3</sub>-MeOH, 10:1, afforded 0.34 g (59%) of compound **XIX**, mp 120–122°C, [α]<sub>D</sub><sup>20</sup> 35.1° (c 1.0, MeOH). <sup>1</sup>H (CD<sub>3</sub>OD), δ, ppm (*J*, Hz): 0.86 s (3H, H<sub>3</sub>C<sup>18</sup>), 0.96 s (3H, H<sub>3</sub>C<sup>19</sup>), 1.15 s (3H, H<sub>3</sub>C<sup>21</sup>), 1.20 s (6H, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.38–2.09 m (20H, CH<sub>2</sub>), 2.30–2.40 m (2H, HC<sup>5</sup> and HC<sup>17</sup>), 3.14 m (1H, HC<sup>9</sup>, *w*<sub>1/2</sub> 24), 3.57 t (2H, H<sub>2</sub>C<sup>4</sup>, <sup>3</sup>*J* 7), 3.65 m (1H, HC<sup>22</sup>, *w*<sub>1/2</sub> 17), 3.84 m (1H, HC<sup>2</sup>, *w*<sub>1/2</sub> 22), 3.95 m (1H, HC<sup>3</sup>, *w*<sub>1/2</sub> 11), 4.99 m (1H, HC<sup>1</sup>), 5.82 d (1H, HC<sup>7</sup>, <sup>4</sup>*J* 2). <sup>13</sup>C (CD<sub>3</sub>OD), δ, ppm: 17.7 q (C<sup>18</sup>), 21.5 t (C<sup>11</sup>), 22.7 t (C<sup>16</sup>), 23.6 q (C<sup>21</sup>), 24.5 q (C<sup>19</sup>), 24.7 t (C<sup>23</sup>), 28.2 t (C<sup>3</sup>), 29.0 q and 29.6 q (C<sup>26</sup> and C<sup>27</sup>), 31.8 t (C<sup>2</sup>), 32.2 t (C<sup>15</sup>), 32.9 t (C<sup>4</sup> and C<sup>12</sup>), 35.2 d (C<sup>9</sup>), 37.3 t (C<sup>1</sup>), 39.3 s (C<sup>10</sup>), 42.2 t (C<sup>24</sup>), 48.4 s (C<sup>13</sup>), 51.4 d

(C<sup>17</sup>), 51.8 d (C<sup>5</sup>), 62.9 t (C<sup>4</sup>), 68.5 d (C<sup>3</sup>), 68.7 d (C<sup>2</sup>), 71.2 s (C<sup>25</sup>), 85.1 s (C<sup>20</sup>), 85.3 s (C<sup>14</sup>), 85.5 d (C<sup>22</sup>), 105.3 d (C<sup>1</sup>), 122.2 d (C<sup>7</sup>), 167.8 s (C<sup>8</sup>), 206.6 s (C<sup>6</sup>). Found, %: C 67.80; H 9.31. C<sub>31</sub>H<sub>50</sub>O<sub>8</sub>. Calculated, %: C 67.61; H 9.15.

**25-O-Acetyl-2,3:20,22-bis-O-[(1R)-ethylidene]-20-hydroxyecdysone (XX).** To a solution of 0.98 g (1.84 mmol) of compound **XII** in 15 ml of anhydrous pyridine was added 0.56 g (5.49 mmol) of freshly distilled acetic anhydride and 0.1 mg of DMAP, the reaction mixture was stirred for 7 days at 40°C, and then it was evaporated in a vacuum. The residue was subjected to chromatography on a column charged with 50 g of SiO<sub>2</sub> (eluent CHCl<sub>3</sub>-MeOH, 50:1) to obtain 0.99 g (93%) of compound **XX**, mp 95–97°C, [α]<sub>D</sub><sup>23</sup> 37.9° (C 6.60, CHCl<sub>3</sub>). IR spectrum (KBr), ν, cm<sup>-1</sup>: 3450, 1720, 1650. UV spectrum, λ<sub>max</sub>, nm: 242. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm (*J*, Hz): 0.75 s (3H, H<sub>3</sub>C<sup>18</sup>), 0.90 s (3H, H<sub>3</sub>C<sup>19</sup>), 1.08 s (3H, H<sub>3</sub>C<sup>21</sup>), 1.26 d (3H, CH<sub>3</sub>C<sup>11</sup>, <sup>3</sup>*J* 5), 1.32 d (3H, CH<sub>3</sub>C<sup>1</sup>, <sup>3</sup>*J* 5), 1.36 s and 1.38 s (6H, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.89 s (3H, CH<sub>3</sub>CO), 1.20–2.10 m (16H, CH<sub>2</sub>), 2.24 m (1H, HC<sup>17</sup>, *w*<sub>1/2</sub> 24), 2.50 m (1H, HC<sup>5</sup>, *w*<sub>1/2</sub> 24), 2.78 m (1H, HC<sup>9</sup>, *w*<sub>1/2</sub> 25), 3.52 m (1H, HC<sup>22</sup>, *w*<sub>1/2</sub> 12), 4.00 m (1H, HC<sup>3</sup>, *w*<sub>1/2</sub> 10), 4.10 m (1H, HC<sup>2</sup>, *w*<sub>1/2</sub> 20), 4.95 q (1H, HC<sup>1</sup>, <sup>3</sup>*J* 5), 5.02 q (1H, HC<sup>11</sup>, <sup>3</sup>*J* 5), 5.73 br.s (1H, HC<sup>7</sup>, *w*<sub>1/2</sub> 7). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 16.7 q (C<sup>18</sup>), 20.3 t (C<sup>11</sup>), 21.3 t (C<sup>16</sup>), 21.3 q and 21.4 q (CH<sub>3</sub>C<sup>1</sup> and CH<sub>3</sub>C<sup>11</sup>), 22.2 q (CH<sub>3</sub>CO), 22.3 q (C<sup>21</sup>), 23.0 t (C<sup>23</sup>), 23.4 q (C<sup>19</sup>), 25.5 q and 25.9 q (C<sup>26</sup> and C<sup>27</sup>), 26.4 t (C<sup>15</sup>), 30.6 t (C<sup>12</sup>), 31.1 t (C<sup>4</sup>), 34.5 d (C<sup>9</sup>), 37.5 s (C<sup>10</sup>), 38.3 t (C<sup>1</sup>), 38.4 t (C<sup>24</sup>), 47.1 s (C<sup>13</sup>), 49.7 d (C<sup>17</sup>), 50.6 d (C<sup>5</sup>), 71.4 d (C<sup>3</sup>), 73.5 d (C<sup>2</sup>), 81.8 s (C<sup>25</sup>), 83.5 s (C<sup>20</sup>), 83.6 d (C<sup>22</sup>), 84.3 s (C<sup>14</sup>), 100.9 d (C<sup>1</sup>), 101.3 d (C<sup>11</sup>), 120.9 d (C<sup>7</sup>), 163.8 s (C<sup>8</sup>), 170.4 s (MeCO), 202.8 s (C<sup>6</sup>). Found, %: C 69.11; H 8.89. C<sub>33</sub>H<sub>50</sub>O<sub>8</sub>. Calculated, %: C 68.96; H 8.77.

**25-O-Acetyl-2,3:20,22-bis-O-isopropylidene-20-hydroxyecdysone (XXI).** To a solution of 1 g (1.79 mmol) of compound **XIII** in 15 ml of anhydrous pyridine was added 0.55 g (5.39 mmol) of freshly distilled acetic anhydride and 0.1 mg of DMAP, the reaction mixture was stirred for 10 days at 40°C, and then it was evaporated in a vacuum. The residue was subjected to chromatography on a column charged with 50 g of SiO<sub>2</sub> (eluent CHCl<sub>3</sub>-MeOH, 15:1) to obtain 0.93 g (87%) of compound **XXI**, mp 197–198°C (publ.: mp 199–201°C [11]), [α]<sub>D</sub><sup>22</sup> 97.1° (C 1.1, CHCl<sub>3</sub>). IR and <sup>1</sup>H NMR spectra were identical to those previously published [11]. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 16.8 q (C<sup>18</sup>), 20.3 t (C<sup>11</sup>), 21.0 t (C<sup>16</sup>), 21.7 q (C<sup>21</sup>), 22.2 q (CH<sub>3</sub>CO), 23.0 t (C<sup>23</sup>), 23.4 q (C<sup>19</sup>), 25.5 q and 25.9 q (C<sup>26</sup> and C<sup>27</sup>), 26.2 q

\* 1,2-epoxyperfluorooctane was prepared by epoxidation of 1-perfluorooctene by procedure from [18], bp 102–105°C, *n*<sub>D</sub><sup>25</sup> 1.2802, IR spectrum (liquid, thin film), ν, cm<sup>-1</sup>: 1535 (epoxy ring). <sup>13</sup>C (CDCl<sub>3</sub>-C<sub>6</sub>F<sub>6</sub>, 1:1), δ, ppm (*J*, Hz): 92.1 d.m [C<sup>2</sup>, <sup>1</sup>*J*(CF) 287.1], 103.8–123.1 m (C<sup>3</sup>–C<sup>7</sup>), 118.1 q.t [C<sup>8</sup>, <sup>1</sup>*J*(CF) 288.0, <sup>2</sup>*J*(CF) 33.0]. Positive chemical ionization mass spectrum (instrument and procedure of mass spectra measuring see [19]), *m/z* (*I*<sub>rel</sub> %): 457 (0.7) [M + C<sub>3</sub>H<sub>5</sub>]<sup>+</sup>, 445 (23.8) [M + C<sub>2</sub>H<sub>5</sub>]<sup>+</sup>, 417 (100) [M + H]<sup>+</sup>, 397 (13.8) [M – F]<sup>+</sup>, 395 (27.1), 381 (1.5) [C<sub>8</sub>F<sub>15</sub>]<sup>+</sup>, 367 (19), 331 (1.0) [C<sub>7</sub>F<sub>13</sub>]<sup>+</sup>, 319 (1.2), 281 (8.1) [C<sub>6</sub>F<sub>11</sub>]<sup>+</sup>, 231 (2.8) [C<sub>5</sub>F<sub>9</sub>]<sup>+</sup>. Negative chemical ionization mass spectrum, *m/z* (*I*<sub>rel</sub> %): 435 (0.58) [M + F]<sup>-</sup>, 416 (2.1) [M]<sup>-</sup>, 400 (33.6) [M – O]<sup>-</sup>, 378 (1.6) [M – F<sub>2</sub>]<sup>-</sup>, 367 (7.9), 366 (100) [M – CF<sub>2</sub>]<sup>-</sup>, 362 (4.3), 350 (1.5) [M – COF<sub>2</sub>]<sup>-</sup>, 281 (7.2) [C<sub>6</sub>F<sub>11</sub>]<sup>-</sup>, 231 (2.6) [C<sub>5</sub>F<sub>9</sub>]<sup>-</sup>. Electron impact mass spectrum, *m/z* (*I*<sub>rel</sub> %): 416 (0.06) [M]<sup>+</sup>, 397 (4.6) [M – F]<sup>+</sup>, 381 (0.04) [M – F – O]<sup>+</sup>, 347 (0.13) [M – F – CF<sub>2</sub>]<sup>+</sup>, 319 (3.6) [M – FCF<sub>2</sub> – CO]<sup>+</sup>, 281 (11.9) [C<sub>6</sub>F<sub>11</sub>]<sup>+</sup>, 231 (77.9) [C<sub>5</sub>F<sub>9</sub>]<sup>+</sup>, 181 (51.1) [C<sub>4</sub>F<sub>7</sub>]<sup>+</sup>, 169 (33.8), 131 (92.5) [C<sub>3</sub>F<sub>5</sub>]<sup>+</sup>, 119 (46.7), 100 (52.7) [CF<sub>2</sub> = CF<sub>2</sub>]<sup>+</sup>, 69 (100) [CF<sub>3</sub>]<sup>+</sup>.

and 26.6 q ( $\text{Me}_2\text{C}^I$ ), 26.3 t ( $\text{C}^{15}$ ), 28.3 q and 28.8 q ( $\text{Me}_2\text{C}^{II}$ ), 30.8 t ( $\text{C}^{12}$ ), 31.0 t ( $\text{C}^4$ ), 34.2 d ( $\text{C}^9$ ), 37.3 t ( $\text{C}^1$ ), 37.5 s ( $\text{C}^{10}$ ), 38.2 t ( $\text{C}^{24}$ ), 47.3 s ( $\text{C}^{13}$ ), 48.9 d ( $\text{C}^{17}$ ), 50.6 d ( $\text{C}^5$ ), 71.4 d ( $\text{C}^3$ ), 71.9 d ( $\text{C}^2$ ), 81.2 d ( $\text{C}^{22}$ ), 81.9 s ( $\text{C}^{25}$ ), 84.0 s ( $\text{C}^{20}$ ), 84.3 s ( $\text{C}^{14}$ ), 106.6 s ( $\text{C}^I$ ), 108.0 s ( $\text{C}^{II}$ ), 120.9 d ( $\text{C}^7$ ), 164.0 s ( $\text{C}^8$ ), 170.5 s ( $\text{MeCO}$ ), 203.0 s ( $\text{C}^6$ ).

**25-O-Acetyl-2,3-O-[(2RS)-butan-2-ylidene]-20,22-O-[(2R)-butan-2-ylidene]-20-hydroxyecdysone (XXII) and 2,3:20,22-bis-O-[(2R)-butan-2-ylidene]-20-hydroxyecdysone (R-XIV).** To a solution of 0.90 g (1.53 mmol) of *RS*-isomer of compound XIV in 4 ml of anhydrous pyridine was added 0.93 g (9.12 mmol) of freshly distilled acetic anhydride and 0.1 mg of DMAP, the reaction mixture was stirred for 5 days at room temperature, then evaporated in a vacuum. The residue was subjected to chromatography on a column charged with 50 g of  $\text{SiO}_2$  (eluent  $\text{CHCl}_3$ -MeOH, 40:1) to obtain 0.72 g (75%) of compound XXII,  $R_f$  0.5 ( $\text{CHCl}_3$ -MeOH, 12:1), and 0.11 g (12%) of compound R-XIV,  $R_f$  0.3 ( $\text{CHCl}_3$ -MeOH, 12:1).

**Compound (XXII).** mp 115–118°C,  $[\alpha]_D^{25}$  94.0° ( $\text{C}$  0.61,  $\text{CHCl}_3$ ), IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 3450, 1720, 1650. UV spectrum,  $\lambda_{\text{max}}$ , nm: 241.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm ( $J$ , Hz): 0.72 s (3H,  $\text{H}_3\text{C}^{18}$ ), 0.80–1.00 m (6H,  $\text{CH}_3\text{CH}_2\text{C}^I$  and  $\text{CH}_3\text{CH}_2\text{C}^{II}$ ), 0.91 s (3H,  $\text{H}_3\text{C}^{19}$ ), 1.10 s (3H,  $\text{H}_3\text{C}^{21}$ ), 1.19 s (3H,  $\text{H}_3\text{CC}^I$ ), 1.36 s (6H,  $\text{H}_3\text{C}^{26}$  and  $\text{H}_3\text{C}^{27}$ ), 1.39 s (3H,  $\text{H}_3\text{CC}^{II}$ ), 1.90 s (3H,  $\text{CH}_3\text{CO}$ ), 1.00–2.05 m (20H,  $\text{CH}_2$ ), 2.10–2.30 m (2H,  $\text{HC}^5$  and  $\text{HC}^{17}$ ), 2.78 m (1H,  $\text{HC}^9$ ,  $w_{1/2}$  17), 3.57 m (1H,  $\text{HC}^{22}$ ,  $w_{1/2}$  14), 4.12–4.23 m (2H,  $\text{HC}^2$  and  $\text{HC}^3$ ), 5.74 br.s (1H,  $\text{HC}^7$ ,  $w_{1/2}$  7).  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 8.8 q and 8.9 q ( $\text{CH}_3\text{CH}_2\text{C}^I$  and  $\text{CH}_3\text{CH}_2\text{C}^{II}$ ), 16.8 q ( $\text{C}^{18}$ ), 20.4 t ( $\text{C}^{11}$ ), 21.1 t ( $\text{C}^{16}$ ), 22.1 q ( $\text{C}^{21}$ ), 22.3 q ( $\text{CH}_3\text{CO}$ ), 23.1 t ( $\text{C}^{23}$ ), 23.4 q and 23.6 q ( $\text{H}_3\text{CC}^I$  and  $\text{H}_3\text{CC}^{II}$ ), 25.2 q ( $\text{C}^{19}$ ), 25.6 q and 26.0 q ( $\text{C}^{26}$  and  $\text{C}^{27}$ ), 30.9 t ( $\text{C}^{15}$ ), 31.2 t ( $\text{C}^{12}$ ), 32.2 t ( $\text{C}^4$ ), 34.3 d ( $\text{C}^9$ ), 34.8 t ( $\text{C}^1$ ), 37.5 t ( $\text{H}_2\text{CC}^I$  and  $\text{H}_2\text{CC}^{II}$ ), 37.6 s ( $\text{C}^{10}$ ), 38.0 t ( $\text{C}^{24}$ ), 47.3 s ( $\text{C}^{13}$ ), 49.2 d ( $\text{C}^{17}$ ), 50.7 d ( $\text{C}^5$ ), 71.0 d, 71.5 d and 71.6 d ( $\text{C}^2$  and  $\text{C}^3$ ), 81.0 d ( $\text{C}^{22}$ ), 82.0 s ( $\text{C}^{25}$ ), 83.6 s ( $\text{C}^{20}$ ), 84.5 s ( $\text{C}^{14}$ ), 108.6 s ( $\text{C}^I$ ), 110.1 s and 110.2 s ( $\text{C}^{II}$ ), 121.0 d ( $\text{C}^7$ ), 163.8 s ( $\text{C}^8$ ), 170.5 s ( $\text{MeCO}$ ), 203.1 s ( $\text{C}^6$ ). Found, %: C 70.67; H 9.45.  $\text{C}_{37}\text{H}_{58}\text{O}_8$ . Calculated, %: C 70.44; H 9.27.

**Compound (R-XIV).** mp 119–120°C,  $[\alpha]_D^{28}$  9.4° ( $\text{C}$  11.46,  $\text{CHCl}_3$ ). IR, UV,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (solvent  $\text{CDCl}_3$ ) were identical to those reported for compound XIV, except for signals: 4.21 m (2H,  $\text{HC}^2$  and  $\text{HC}^3$ ,  $w_{1/2}$  12) ( $^1\text{H}$ ) and signals: 37.7 t ( $\text{C}^1$ ), 50.7 d ( $\text{C}^5$ ), 71.6 d and 72.0 d ( $\text{C}^2$  and  $\text{C}^3$ ), and 110.4 s ( $\text{C}^{II}$ ) ( $^{13}\text{C}$ ).

**25-O-Acetyl-20,22-O-[(1R)-ethylidene]-20-hydroxyecdysone (XXIII).** Stirring of 70 mg (0.12 mmol) of compound XX and 3 ml of 70% acetic acid at room temperature was carried out till complete conversion of the substrate (48 h, TLC monitoring). The reaction mixture was diluted with water (3 ml), the reaction product was extracted with ethyl ether (3×5 ml), the combined extracts were washed with a saturated NaCl solution and evaporated in a vacuum. The residue was subjected to chromatography on a column charged with 3 g of  $\text{SiO}_2$  (eluent  $\text{CHCl}_3$ ) to obtain 66 mg (94%) of compound XXIII, mp 120–122°C,  $[\alpha]_D^{23}$  40.0° ( $\text{C}$  6.45,  $\text{CHCl}_3$ ). IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 3450, 1720, 1650. UV spectrum,  $\lambda_{\text{max}}$ , nm: 242.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm ( $J$ , Hz): 0.81 s (3H,  $\text{H}_3\text{C}^{18}$ ), 0.95 s (3H,  $\text{H}_3\text{C}^{19}$ ), 1.12 s (3H,  $\text{H}_3\text{C}^{21}$ ), 1.33 d (3H,  $\text{H}_3\text{CC}^I$ ,  $^3J$  5.0), 1.43 s and 1.45 s (6H,  $\text{H}_3\text{C}^{26}$  and  $\text{H}_3\text{C}^{27}$ ), 1.96 s (3H,  $\text{CH}_3\text{CO}$ ), 1.20–2.10 m (16H,  $\text{CH}_2$ ), 2.26 d.d (1H,  $\text{HC}^{17}$ ,  $^3J$  8.0 and 7.5), 2.39 d.d (1H,  $\text{HC}^5$ ,  $^3J$  13.0 and 3.0), 3.04 m (1H,  $\text{HC}^9$ ,  $w_{1/2}$  23), 3.58 d.d (1H,  $\text{HC}^{22}$ ,  $^3J$  7.5 and 2.0), 3.86 m (1H,  $\text{HC}^2$ ,  $w_{1/2}$  22), 3.97 m (1H,  $\text{HC}^3$ ,  $w_{1/2}$  10), 5.03 q and 5.27 q ( $1R/1'S \sim 95:5$ ) (1H,  $\text{HC}^I$ ,  $^3J$  5.0), 5.81 br.s (1H,  $\text{HC}^7$ ,  $w_{1/2}$  6).  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 17.0 q ( $\text{C}^{18}$ ), 20.4 t ( $\text{C}^{11}$ ), 21.5 t ( $\text{C}^{16}$ ), 21.6 q ( $\text{H}_3\text{CC}^I$ ), 22.4 q ( $\text{CH}_3\text{CO}$ ), 23.0 q ( $\text{C}^{21}$ ), 23.2 t ( $\text{C}^{23}$ ), 23.9 q ( $\text{C}^{19}$ ), 25.7 q and 26.2 q ( $\text{C}^{26}$  and  $\text{C}^{27}$ ), 30.8 t ( $\text{C}^{15}$ ), 31.4 t ( $\text{C}^{12}$ ), 31.5 t ( $\text{C}^4$ ), 33.8 d ( $\text{C}^9$ ), 36.6 t ( $\text{C}^1$ ), 38.2 s ( $\text{C}^{10}$ ), 38.5 t ( $\text{C}^{24}$ ), 47.1 s ( $\text{C}^{13}$ ), 50.0 d ( $\text{C}^5$  and  $\text{C}^{17}$ ), 67.3 d ( $\text{C}^3$ ), 67.7 d ( $\text{C}^2$ ), 82.0 s ( $\text{C}^{25}$ ), 83.7 s ( $\text{C}^{20}$ ), 83.8 d ( $\text{C}^{22}$ ), 84.6 s ( $\text{C}^{14}$ ), 101.1 d ( $\text{C}^I$ ), 121.4 d ( $\text{C}^7$ ), 165.4 s ( $\text{C}^8$ ), 170.6 s ( $\text{MeCO}$ ), 204.4 s ( $\text{C}^6$ ). Found, %: C 68.03; H 8.98.  $\text{C}_{31}\text{H}_{48}\text{O}_8$ . Calculated, %: C 67.86; H 8.82.

**25-O-Acetyl-20,22-O-isopropylidene-20-hydroxyecdysone (XXIV).** Stirring of 0.2 g (0.32 mmol) of compound XXI and 1 ml of 70% acetic acid at room temperature was carried out till complete conversion of the substrate (3 h, TLC monitoring). The reaction mixture was diluted with water (3 ml), the reaction product was extracted with 1-butanol (3×5 ml), the combined extracts were washed with a saturated NaCl solution and evaporated in a vacuum. The residue was subjected to chromatography on a column charged with 20 g of  $\text{SiO}_2$  (eluent  $\text{CHCl}_3$ -MeOH, 12:1) to obtain 0.18 g (97%) of compound XXIV, mp 203–206°C (publ.: mp 206–208°C [11]),  $[\alpha]_D^{22}$  91.7° ( $\text{C}$  1.2,  $\text{CHCl}_3$ ). IR and  $^1\text{H}$  NMR spectra are identical with the previously reported data [11].  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 17.1 q ( $\text{C}^{18}$ ), 20.4 t ( $\text{C}^{11}$ ), 21.2 t ( $\text{C}^{16}$ ), 21.9 q ( $\text{C}^{21}$ ), 22.4 q ( $\text{CH}_3\text{CO}$ ), 23.3 q ( $\text{C}^{19}$ ), 23.9 t ( $\text{C}^{23}$ ), 25.8 t ( $\text{C}^{15}$ ), 26.2 q ( $\text{C}^{26}$ ), 26.9 q ( $\text{C}^{27}$ ), 29.0 q ( $\text{Me}_2\text{C}^I$ ), 31.5 t ( $\text{C}^{12}$ ), 33.8 t ( $\text{C}^4$ ), 34.8 d



(C<sup>9</sup>), 36.7 t (C<sup>1</sup>), 38.2 s (C<sup>10</sup>), 38.4 t (C<sup>24</sup>), 47.3 s (C<sup>13</sup>), 49.2 d (C<sup>17</sup>), 50.0 d (C<sup>5</sup>), 67.3 d (C<sup>3</sup>), 67.7 d (C<sup>2</sup>), 81.4 d (C<sup>22</sup>), 82.1 s (C<sup>25</sup>), 84.2 s (C<sup>20</sup>), 84.7 s (C<sup>14</sup>), 106.8 s (C<sup>1</sup>), 121.4 d (C<sup>7</sup>), 165.2 s (C<sup>8</sup>), 170.6 s (MeCO), 204.2 s (C<sup>6</sup>).

**25-O-Acetyl-20,22-O-[(2R)-butan-2-ylidene]-20-hydroxyecdysone (XXV).** Stirring of 0.2 g (0.32 mmol) of compound **XXII** and 1 ml of 70% acetic acid at room temperature was carried out till complete conversion of the substrate (3 h, TLC monitoring). The reaction mixture was diluted with water (3 ml), the reaction product was extracted with 1-butanol (3×5 ml), the combined extracts were washed with a saturated NaCl solution and evaporated in a vacuum. The residue was subjected to chromatography on a column charged with 10 g of SiO<sub>2</sub> (eluent CHCl<sub>3</sub>–MeOH, 12:1) to obtain 0.17 g (92%) of compound **XXV**, mp 110–112°C, [α]<sub>D</sub><sup>23</sup> 29.5° (C 2.15, CHCl<sub>3</sub>). IR spectrum (KBr), ν, cm<sup>-1</sup>: 3450, 1720, 1650. UV spectrum, λ<sub>max</sub>, nm: 243. <sup>1</sup>H NMR spectrum (C<sub>5</sub>D<sub>5</sub>N), δ, ppm (J, Hz): 0.95 s (3H, H<sub>3</sub>C<sup>18</sup>), 1.03–1.10 m (3H, H<sub>3</sub>CCH<sub>2</sub>C<sup>11</sup>), 1.06 s (3H, H<sub>3</sub>C<sup>19</sup>), 1.32 s (3H, H<sub>3</sub>C<sup>21</sup>), 1.39 s (3H, H<sub>3</sub>CC<sup>11</sup>), 1.43 s and 1.44 s (6H, H<sub>3</sub>C<sup>26</sup> and H<sub>3</sub>C<sup>27</sup>), 1.91 s (3H, CH<sub>3</sub>CO), 1.20–2.55 m (18H, CH<sub>2</sub>), 2.73 d.d (1H, HC<sup>17</sup>, <sup>3</sup>J 7.5 and 7.0), 2.98 d.d (1H, HC<sup>5</sup>, <sup>3</sup>J 10.0 and 3.0), 3.54 m (1H, HC<sup>9</sup>, w<sub>1/2</sub> 25), 3.91 d.d (1H, HC<sup>22</sup>, <sup>3</sup>J 7.0 and 2.0), 4.14 m (1H, HC<sup>2</sup>, w<sub>1/2</sub> 23), 4.21 m (1H, HC<sup>3</sup>, w<sub>1/2</sub> 11), 6.22 br.s (1H, HC<sup>7</sup>, w<sub>1/2</sub> 7). <sup>13</sup>C NMR spectrum (C<sub>5</sub>D<sub>5</sub>N), δ, ppm: 9.4 q (H<sub>3</sub>CCH<sub>2</sub>C<sup>11</sup>), 17.1 q (C<sup>18</sup>), 20.9 t (C<sup>11</sup>), 21.9 t (C<sup>16</sup>), 22.1 q (CH<sub>3</sub>CO), 22.5 q (C<sup>21</sup>), 23.6 t (C<sup>23</sup>), 23.9 q (C<sup>19</sup>), 24.3 q (H<sub>3</sub>CC<sup>11</sup>), 25.7 q and 25.8 q (C<sup>26</sup> and C<sup>27</sup>), 29.8 t (C<sup>15</sup>), 31.4 t (C<sup>12</sup>), 31.5 t (C<sup>4</sup>), 34.4 d (C<sup>9</sup>), 35.4 t (H<sub>2</sub>CC<sup>11</sup>), 37.8 t (C<sup>1</sup>), 38.5 s (C<sup>10</sup>), 38.7 t (C<sup>24</sup>), 47.7 C (C<sup>13</sup>), 49.9 d (C<sup>17</sup>), 51.2 d (C<sup>5</sup>), 67.9 d (C<sup>3</sup>), 68.0 d (C<sup>2</sup>), 81.6 d (C<sup>22</sup>), 81.7 s (C<sup>25</sup>), 83.9 s (C<sup>20</sup>), 84.5 s (C<sup>14</sup>), 108.8 s (C<sup>1</sup>), 121.6 d (C<sup>7</sup>), 165.4 s (C<sup>8</sup>), 170.1 s (MeCO), 203.3 s (C<sup>6</sup>). Found, %: C 68.98; H 9.25. C<sub>33</sub>H<sub>52</sub>O<sub>8</sub>. Calculated, %: C 68.72; H 9.09.

**Viticosterone E, or 25-O-acetyl-20-hydroxyecdysone, or (20R,22R)-2β,3β,14α,20,22-penta-hydroxy-25-acetoxy-5β-cholest-7-eh-6-one (XXVI).** (a) Stirring of 0.1 g (0.18 mmol) of compound **XXIII** and 1 ml of 70% ACOH was performed for 1.5 h at room temperature, then 85 mg of ZnCl<sub>2</sub> was added, and the stirring was continued for 5 h more. Then the reaction mixture was diluted with water (3 ml), the reaction product was extracted with 1-butanol (3×10 ml), the combined extracts were washed with a saturated NaCl solution, dried on MgSO<sub>4</sub>, and evaporated in a vacuum. The residue was subjected to chromatography on a column

charged with SiO<sub>2</sub> (eluent CHCl<sub>3</sub>–MeOH, 30:1) to obtain 90 mg (96%) of compound **XXVI**, mp 195–196°C, [α]<sub>D</sub><sup>20</sup> 56.1° (C 0.80, MeOH). Pubtd.: mp 198–199°C, [α]<sub>D</sub><sup>20</sup> 60.0° (C 1.31, MeOH) [4]. IR, UV, <sup>1</sup>H and <sup>13</sup>C NMR spectra (solvent CDCl<sub>3</sub>) were identical to those reported IR, UV, and <sup>1</sup>H NMR spectra were identical to those reported before [4]. <sup>13</sup>C NMR spectrum (C<sub>5</sub>D<sub>5</sub>N), δ, ppm: 17.6 q (C<sup>18</sup>), 20.8 t (C<sup>11</sup>), 21.2 t (C<sup>16</sup>), 21.3 q (C<sup>21</sup>), 22.0 q (CH<sub>3</sub>CO), 24.2 q (C<sup>19</sup>), 25.9 q and 26.1 q (C<sup>26</sup> and C<sup>27</sup>), 26.6 t (C<sup>23</sup>), 31.4 t (C<sup>4</sup>), 31.8 t (C<sup>15</sup>), 32.2 t (C<sup>12</sup>), 34.2 d (C<sup>9</sup>), 37.6 t (C<sup>1</sup>), 38.4 s (C<sup>10</sup>), 39.0 t (C<sup>24</sup>), 47.8 s (C<sup>13</sup>), 49.9 d (C<sup>17</sup>), 51.1 d (C<sup>5</sup>), 67.8 d (C<sup>3</sup>), 67.9 d (C<sup>2</sup>), 76.6 s (C<sup>20</sup>), 77.2 d (C<sup>22</sup>), 82.2 s (C<sup>25</sup>), 83.9 s (C<sup>14</sup>), 121.4 d (C<sup>7</sup>), 165.9 s (C<sup>8</sup>), 170.1 s (MeCO<sub>2</sub>), 203.4 s (C<sup>6</sup>).

(b) From 0.1 g (0.17 mmol) of compound **XXIV** under conditions of procedure *a* we obtained 36 mg (41%) of compound **XXVI** identical to that obtained in the experiment (a).

(c) From 0.1 g (0.17 mmol) of compound **XXV** under conditions of procedure *a* we obtained 41 mg (46%) of compound **XXVI** identical to that obtained in the experiment (a).

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