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# Synthesis and Transformations of 2β,3β-Diacetoxy-20-(4,5-dihydroisoxazol-5-yl)-6-oxo Steroids

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**Abstract**—20-Hydroxy-20-(4,5-dihydroisoxazol-5-yl) steroid was brought into reactions typical of functionalization of rings A and B in ecdysteroids. The dihydroisoxazole ring remained unchanged in reactions leading to formation of the 2β,3β-dihydroxy-6-oxo moiety. The isomerization of 5α-bromo derivative in acetic acid in the presence of a catalytic amount of hydrobromic acid and Lewis acids is accompanied by elimination of the hydroxy group from $C^{20}$ and subsequent migration of the double bond to the heteroring to afford the corresponding isoxazole derivative.

Steroid compounds having a side-chain dihydroisoxazole ring were successfully used in the synthesis of brassinosteroids, vitamin D precursors, and sapogenins [1–3]. Jiang *et al*. [4] recently reported on the synthesis of 26,27-hexafluoro derivatives of polyhydroxy steroids on the basis of dihydroisoxazolyl steroids [4]. 20-Hydroxy-20-(4,5-dihydroisoxazol-5-yl) derivatives are convenient intermediate products for building up side chains in a series of 20,22,24-trihydroxy steroids, in particular ponasterone C and pterosterone [5]. The goal of the present work was to elucidate the possibility of using 20-hydroxy-20-(4,5-dihydroisoxazol-5-yl) steroids for modification of rings A and B, specifically for introduction of functional groups typical of ecdysteroids. As starting compound we selected 20-hydroxy-20-(4,5-dihydroisoxazol-5-yl) derivative **III** which was prepared in two steps from pregnenolone (**I**) according to the procedure described in [6]. 1,3-Dipolar cycloaddition of isobutyronitrile oxide to compound **II** was characterized by high stereoselectivity, and a mixture of diastereoisomers with respect to $C^{5'}$ was formed at a ratio of 6:1 (according to the $^1$H NMR data). The major isomer **III** was isolated by crystallization. The configuration of the new chiral center was determined on the basis of characteristic proton signals in the $^1$H NMR spectrum, which were identified previously using the X-ray diffraction data for structurally related compounds [7].

Successive tosylation of the 3-hydroxy group in **III**, isosteroid rearrangement, and oxidation afforded ketone **IV** which was subjected to isomerization into compound **V** by the action of pyridinium hydrobromide [8]. Hydroxylation of $\Delta^2$-6-oxo derivative **V** according to Woodward (by the action of silver acetate and iodine in aqueous acetic acid at 50°C) gave 2β-hydroxy-3β-acetoxy steroid **VI**, and acetylation of the latter with acetic anhydride in pyridine resulted in formation of 2β,3β-diacetoxy-6-oxo derivative **VII**. In the *cis*-hydroxylation stage, we also isolated a minor product (~5%) which showed a positive test for halogen; in keeping with published data [9], this product was 2α-iodo-3β-acetoxy derivative; however, its further transformations were beyond the scope of the present study. The structure of 2β,3β-diacetoxy-6-oxo derivative **VII** is confirmed by the presence in its $^1$H NMR spectrum of signals from 2-H and 3-H at δ 5.30 and 4.80 ppm, which correspond to α-oriented protons in the geminal positions with respect to the acetoxy groups [10]. The IR spectrum of **VII** contained absorption bands belonging to stretching vibrations of the hydroxy group (3520 $cm^{-1}$), two acetyl groups (1765, 1750 and 1255, 1245 $cm^{-1}$), and 6-oxo group (1735 $cm^{-1}$). The high-resolution mass spectrum of compound **VII** was also consistent with the assumed structure.

Thus we can conclude that the dihydroisoxazole ring in **III** is stable under conditions of Woodward's hydroxylation and hence in all reactons leading to formation of a 2β,3β-dihydroxy-6-oxo moiety in steroid molecule.

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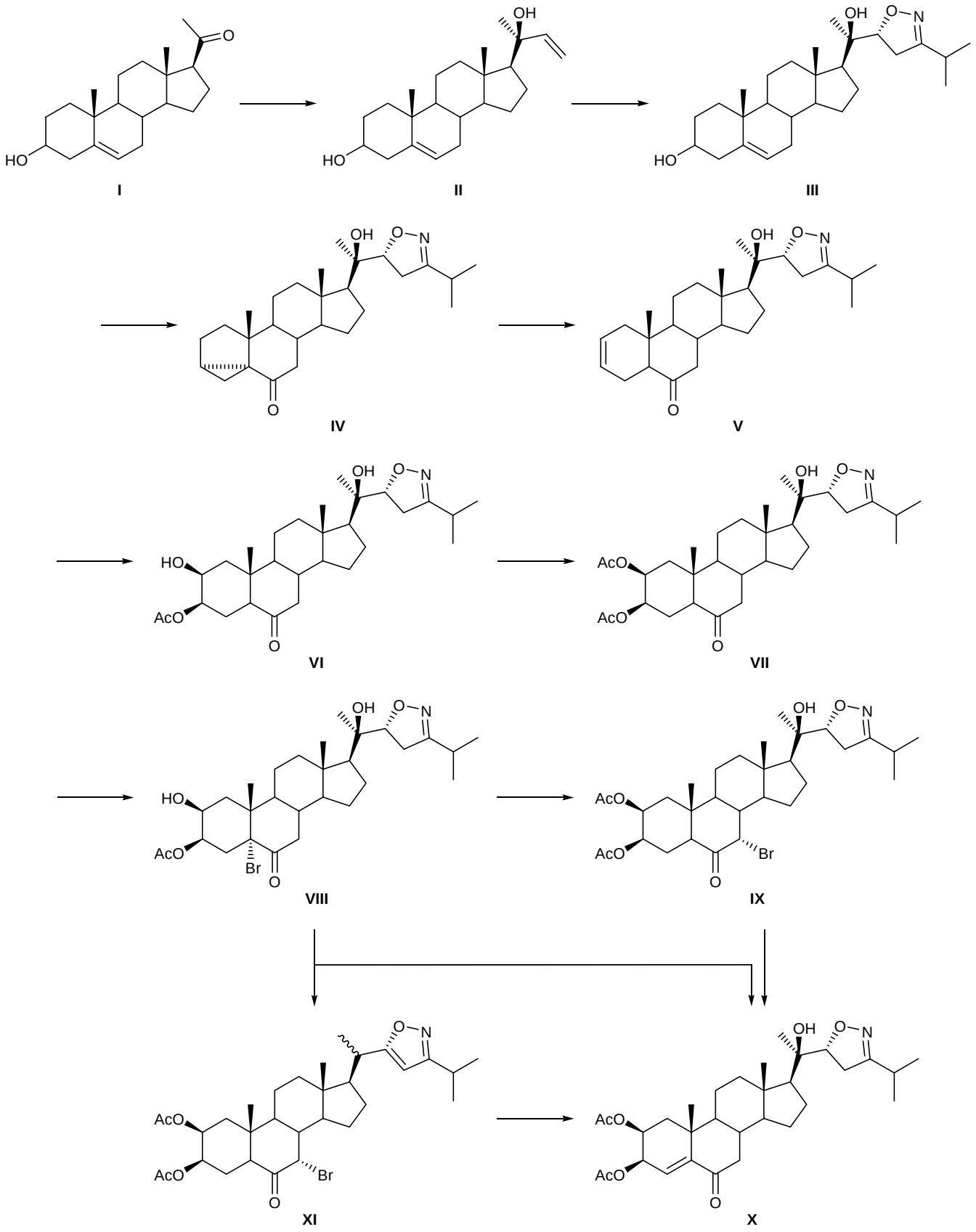
**Scheme 1.**


HO
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VII
HO
AcO
Br
O
VIII
OH
O
N
AcO
AcO
Br
O
IX
AcO
AcO
Br
O
XI
OH
O
N
AcO
AcO
O
X

Unexpectedly, traditional procedures for introduction of $\Delta^7$-double bond into molecule **VII** gave unusual results. Ketone **VII** was treated with bromine in a mixture of acetic acid and dilute hydrobromic acid. However, isomerization of 5α-bromo derivative **VIII** thus obtained into 7α-bromo isomer **IX** by the action of concentrated hydrobromic acid in glacial acetic acid, and subsequent dehydrobromination of **IX** with a mixture of lithium carbonate and lithium bromide in boiling DMF were characterized by low yields, and the product was $\Delta^4$-6-oxo derivative **X** rather than the expected $\Delta^7$-6-oxo steroid. Compound **X** was formed in high yield by dehydrobromination (under the same conditions) of 5α-bromo derivative **VIII**.

In order to improve the yield of 7α-bromo derivative **IX** in the rearrangement of 5α-bromo isomer **VIII**, we tried Lewis acids, in particular zinc bromide. Heating of **VIII** in acetic acid in the presence of catalytic amounts of hydrobromic acid and zinc bromide resulted in elimination of the hydroxy group from $C^{20}$, followed by migration of the emerging double bond to the heteroring. The product was 2β,3β-diacetoxy-7α-bromo-6-oxo derivative **XI** as a mixture of two diastereoisomers with respect to $C^{20}$ (20*R*:20*S* ≈ 5:2; according to the $^1$H NMR data). Compound **XI** showed in the $^1$H NMR spectrum a one-proton doublet at δ 4.16 ppm, which is typical of β-oriented proton on $C^7$, and a multiplet at δ 3.34 ppm due to 5α-H. The structure of the side chain was readily established by comparing the $^1$H NMR spectrum of **XI** with those of structurally related compounds [11, 12]. It should be noted that analogous transformation of 20-hydroxy-20-(4,5-dihydroisoxazol-5-yl) steroids on heating in boiling nitromethane in the presence of trifluoroacetic acid and lithium perchlorate [11] was characterized by a higher yield and was stereoselective.

The results of the present study indicate that classical procedures for ecdysteroid-like functionalization of rings A and B cannot be applied to steroids possessing a dihydroisoxazole ring in the side chain. An alternative way may include initial building up of the 2β,3β-dihydroxy-6-oxo-$\Delta^7$ fragment in pregnane and subsequent attachment of side chain through the corresponding dihydroisoxazole derivatives.

## EXPERIMENTAL

The melting points were determined on a Kofler device. The IR spectra were recorded on a UR-20 spectrometer in the range from 700 to 3600 cm$^{-1}$ from samples prepared as thin films or KBr pellets. The UV spectra were measured on a Specord M-400 spectrophotometer from solutions in methanol. The mass spectra (electron impact, 70 eV) were obtained on a Micromass MasSpec spectrometer. The $^1$H NMR spectra were recorded on a Bruker AC-E 200 instrument (200 MHz) from solutions in chloroform-*d* using TMS as internal reference. The progress of reactions was monitored by TLC on Silufol UV-254 and Kieselgel 60 $F_{254}$ (Merck) plates. Kieselgel 60 silica gel (40–60 μm, Merck) was used for preparative chromatography.

**(20*S*)-24-Norcholesta-5,22-diene-3,20-diol (II).** A preliminarily calcined three-necked flask was charged in a stream of argon with 1.7 g (70 mmol) of magnesium turnings, a few crystals of iodine were added, the flask was heated, 200 ml of THF was added, the mixture was cooled to 0°C, and a solution of 5 ml of vinyl bromide in 75 ml of THF was added dropwise under stirring. A solution of 3.17 g (10 mmol) of pregnenolone (**I**) in 50 ml of THF was then added, and the mixture was stirred for 2 h at room temperature, treated with a saturated solution of ammonium chloride, and extracted with diethyl ether. The extract was dried over sodium sulfate, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using toluene–ethyl acetate as eluent. Yield 3.1 g (92%), mp 132–133°C (from ethyl acetate). IR spectrum, ν, cm$^{-1}$: 3440, 905. $^1$H NMR spectrum, δ, ppm: 0.84 s (3H, 18-Me), 1.02 s (3H, 19-Me), 1.34 s (3H, 21-Me), 3.52 m (1H, 3-H), 4.96 d.d (1H, 23-H, $J_1$ = 1.5, $J_2$ = 10 Hz), 5.15 d.d (1H, 23-H, $J_1$ = 1.5, $J_2$ = 17 Hz), 5.36 m (1H, 6-H), 6.00 d.d (1H, 22-H, $J_1$ = 10, $J_2$ = 17 Hz).

**(5'*R*,20*R*)-20-(3-Isopropyl-4,5-dihydroisoxazol-5-yl)pregn-5-ene-3,20-diol (III).** Pyridine, 0.5 ml, was added under stirring to a suspension of 8 g (60 mmol) of *N*-chlorosuccinimide in 10 ml of chloroform, and 6 g (65 mmol) of isobutyraldehyde oxime was then added dropwise over a period of 15 min. The mixture was stirred for 30 min until a transparent solution was formed, 6 g (17.4 mmol) of compound **II** was added, the mixture was stirred for 30 min, a solution of 6 ml of triethylamine in 30 ml of chloroform was added very slowly (over a period of 4 h), and the mixture was stirred for 10–12 h at room temperature, poured into water, and extracted with chloroform. The extract was dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was subjected to column chromatography on silica gel using toluene–ethyl

acetate (5:1 to 10:1) as eluent. Yield 7.01 g (94%), mp 200–201°C (from methanol). IR spectrum, ν, $cm^{-1}$: 3440, 1485, 1390. $^1H$ NMR spectrum, δ, ppm: 0.84 s (3H, 18-Me), 1.02 s (3H, 19-Me), 1.16 s (3H, 21-Me), 1.18 d (6H, CH**Me**$_2$, $J$ = 7 Hz), 2.70 m (1H, C**H**Me$_2$), 2.84 d (2H, 4-H, $J$ = 10 Hz), 3.54 m (1H, 3-H), 4.50 t (1H, 5'-H, $J$ = 10 Hz), 5.36 m (1H, 6-H).

**(5'*R*,20*R*)-20-Hydroxy-20-(3-isopropyl-4,5-dihydroisoxazol-5-yl)-3α,5-cyclo-5α-pregnan-6-one (IV).** Hydroxy steroid **III**, 5 g (11.66 mmol), was dissolved in 50 ml of anhydrous pyridine, and 5 g (26.26 mmol) of *p*-toluenesulfonyl chloride was added to the solution. The mixture was kept for 14 h at room temperature and poured into 1 l of ice water, and the precipitate was filtered off and washed with water. The crude product was dissolved in 0.8 l of acetone, 5 g of potassium acetate was added, and the mixture was heated for 5 h under reflux. It was then cooled, 40 ml of a 8 N solution of chromic acid (Jones' reagent) was added, and the mixture was stirred for 10 min, diluted with 50 ml of isopropyl alcohol, and filtered through a layer of aluminum oxide. The filtrate was evaporated, and the residue was subjected to column chromatography on silica gel using toluene–ethyl acetate (5:1) as eluent. Yield of oxo steroid **IV** 3.7 g (75%), mp 182–184°C (from petroleum ether–ethyl acetate). IR spectrum, ν, $cm^{-1}$: 3570, 1700, 1480, 1395. $^1H$ NMR spectrum, δ, ppm: 0.90 s (3H, 18-Me), 1.04 s (3H, 19-Me), 1.16 s (3H, 21-Me), 1.18 d (6H, CH**Me**$_2$, $J$ = 7 Hz), 2.72 m (1H, C**H**Me$_2$), 2.84 d (2H, 4'-H, $J$ = 10 Hz), 4.50 t (1H, 5'-H, $J$ = 10 Hz). Mass spectrum, *m*/*z*: 428 $[M + 1]^+$, 409 $[M - H_2O]^+$, 396 $[M - H_2O - Me]^+$, 315 $[M$ – dihydroisoxazole$]^+$, 297 $[M - H_2O$ – dihydroisoxazole$]^+$.

**(5'*R*,20*R*)-20-Hydroxy-20-(3-isopropyl-4,5-dihydroisoxazol-5-yl)pregn-2-en-6-one (V).** Compound **IV**, 1.9 g (4.45 mmol), was dissolved in 20 ml of dimethylformamide, 2.5 g of pyridine hydrobromide was added, and the mixture was heated under argon for 1.5 h at the boiling point, treated with water (200 ml), and extracted with chloroform. The organic phase was washed with 5% hydrochloric acid and dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using toluene–ethyl acetate (5:1) as eluent. Yield 1.3 g (68%), mp 178–180°C (from methanol). IR spectrum, ν, $cm^{-1}$: 3570, 1725, 1480, 1395. $^1H$ NMR spectrum, δ, ppm: 0.71 s (3H, 18-Me), 0.83 s (3H, 19-Me), 1.16 s (3H, 21-Me), 1.18 d (6H, CH**Me**$_2$, $J$ = 7 Hz), 2.70 m (1H, C**H**Me$_2$), 2.84 d (2H, 4'-H, $J$ = 10 Hz), 4.50 t (1H, 5'-H, $J$ = 10 Hz), 5.56 m (1H, 3-H), 5.69 m (1H, 2-H). Mass spectrum, *m*/*z*: 428 $[M + 1]^+$, 315 $[M$ – dihydroisoxazole$]^+$, 297 $[M - H_2O$ – dihydroisoxazole$]^+$.

**(5'*R*,20*R*)-3β-Acetoxy-2β,20-dihydroxy-20-(3-isopropyl-4,5-dihydroisoxazol-5-yl)pregnan-6-one (VI).** Silver acetate, 1.5 g, was added to a solution of 1.3 g (3.05 mmol) of compound **V** in 104 ml of a 25:1 acetic acid–water mixture, the mixture was heated to 50°C, and 1 g of powdered iodine was added with stirring. The mixture was stirred for 20 min at 50–60°C, the precipitate was filtered off and washed with ethyl acetate, and the filtrate was dried over sodium sulfate and evaporated. The residue was subjected to chromatography on silica gel using toluene–ethyl acetate (7:1) as eluent. Yield 0.822 g (55%), mp 195–197°C (from ethyl acetate). IR spectrum, ν, $cm^{-1}$: 3480, 1735, 1715, 1480, 1395, 1250. $^1H$ NMR spectrum, δ, ppm: 0.82 s (3H, 18-Me), 0.88 s (3H, 19-Me), 1.16 s (3H, 21-Me), 1.18 d (6H, CH**Me**$_2$, $J$ = 7 Hz), 2.10 s (3H, OAc), 2.70 m (1H, C**H**Me$_2$), 2.84 d (2H, 4'-H, $J$ = 10 Hz), 3.69 m (1H, 2-H), 4.50 t (1H, 5'-H, $J$ = 10 Hz), 5.15 m (1H, 3-H).

**(5'*R*,20*R*)-2β,3β-Diacetoxy-20-hydroxy-20-(3-isopropyl-4,5-dihydroisoxazol-5-yl)pregnan-6-one (VII).** Compound **VI**, 0.5 g (1.02 mmol), was dissolved in 5 ml of pyridine, 3 ml of acetic anhydride was added to the solution, and the mixture was left overnight at room temperature. The mixture was poured into water, and the precipitate was filtered off and dried for 2 h at 40°C under reduced pressure. Yield 0.49 g (92%), mp 205–207°C (from hexane–ethyl acetate). IR spectrum, ν, $cm^{-1}$: 3520, 1745, 1715, 1480, 1370, 1265, 1235. $^1H$ NMR spectrum, δ, ppm: 0.84 s (3H, 18-Me), 0.95 s (3H, 19-Me), 1.16 s (3H, 21-Me), 1.18 d (6H, CH**Me**$_2$, $J$ = 7 Hz), 2.02 s (3H, OCOMe), 2.10 s (3H, OCOMe), 2.70 m (1H, C**H**Me$_2$), 2.84 d (2H, 4'-H, $J$ = 10 Hz), 4.50 t (1H, 5'-H, $J$ = 10 Hz), 4.80 m (1H, 2α-H), 5.30 m (1H, 3α-H). Mass spectrum, *m*/*z*: 546 $[M + 1]^+$, 433 $[M$ – dihydroisoxazole$]^+$, 415 $[M - H_2O$ – dihydroisoxazole$]^+$, 373 $[M$ – AcOH – dihydroisoxazole$]^+$, 331 (100%) $[M$ – AcOH – side chain$]^+$, 313 $[M$ – 2AcOH – dihydroisoxazole$]^+$. Calculated: $[M - H_2O]^+$ 527.3247. $C_{31}H_{45}NO_6$. Found: $(M - H_2O)$ 527.3244.

**(5'*R*,20*R*)-2β,3β-Diacetoxy-5α-bromo-20-hydroxy-20-(3-isopropyl-4,5-dihydroisoxazol-5-yl)-pregnan-6-one (VIII).** A few drops of hydrobromic

acid were added to a mixture of 0.22 g (0.415 mmol) of 6-oxo steroid **VII** and 5 ml of acetic acid, and 0.5 ml (0.5 mmol) of a 1 M solution of bromine in acetic acid was then added dropwise. The mixture was stirred for 2 h at 50°C, poured into ice water (~50 ml), and extracted with ethyl acetate. The extract was washed with a solution of sodium hydrogen carbonate and dried over sodium sulfate, the solvent was distilled off, and the residue was subjected to column chromatography on silica gel using toluene–ethyl acetate (6:1) as eluent. Yield 0.23 g (92%), mp 185–187°C (from ethyl acetate). IR spectrum, ν, $cm^{-1}$: 3520, 1765, 1750 sh, 1735, 1480, 1370, 1255, 1245. $^1$H NMR spectrum, δ, ppm: 0.81 s (3H, 18-Me), 1.18 m (12H, 19-Me, 21-Me, CH**Me**$_2$), 2.02 s (3H, OCOMe), 2.08 s (3H, OCOMe), 2.70 m (1H, C**H**Me$_2$), 2.82 d (2H, 4'-H, $J$ = 10 Hz), 4.48 t (1H, 5'-H, $J$ = 10 Hz), 5.40 m (1H, 2α-H), 5.54 m (1H, 3α-H). Found, %: C 61.32; H 7.73; Br 12.69; N 2.11. $C_{31}H_{46}BrNO_7$. Calculated, %: C 59.61; H 7.42; Br 12.79; N 2.24.

**(5'*R*,20*R*)-2β,3β-Diacetoxy-7α-bromo-20-hydroxy-20-(3-isopropyl-4,5-dihydroisoxazol-5-yl)pregnan-6-one (IX).** Compound **VIII**, 0.1 g (0.19 mmol), was dissolved in 5 ml of glacial acetic acid, 2 drops of 3% hydrobromic acid were added, and the mixture was left to stand for 24 h at room temperature. It was then poured into water, the precipitate was filtered off and dissolved in chloroform, and the solution was dried over sodium sulfate and evaporated. According to the $^1$H NMR data, the residue was a ~1:3 mixture of initial compound **VIII** and 7α-bromo isomer **IX**. A small amount (20 mg) of pure compound **IX** was isolated by column chromatography on silica gel. $^1$H NMR spectrum, δ, ppm: 0.86 s (3H, 18-Me), 0.96 s (3H, 19-Me), 1.14 s (3H, 21-Me), 1.18 d (6H, CH**Me**$_2$, $J$ = 7 Hz), 2.02 s (3H, OCOMe), 2.08 s (3H, OCOMe), 2.70 m (1H, C**H**Me$_2$), 2.82 d (2H, 4'-H, $J$ = 10 Hz), 3.40 d.d (1H, 5α-H, $J_1$ = 12, $J_2$ = 3 Hz), 4.20 d (1H, 7β-H, $J$ = 3 Hz), 4.48 t (1H, 5'-H, $J$ = 10 Hz), 4.88 m (1H, 2α-H), 5.30 m (1H, 3α-H).

**(5'*R*,20*R*)-2β,3β-Diacetoxy-20-hydroxy-20-(3-isopropyl-4,5-dihydroisoxazol-5-yl)pregn-4-en-6-one (X).** A mixture of 7α- and 5α-bromo isomers **IX** and **VIII**, 0.5 g (0.8 mmol), was dissolved in 10 ml of anhydrous dimethylformamide, 0.07 g (0.82 mmol) of lithium bromide and 0.122 g (1.65 mmol) of lithium carbonate were added, and the mixture was heated for 3 h at 125–140°C. The mixture was cooled, poured into water, and filtered, the filtrate was extracted with ethyl acetate, the extract was dried over anhydrous sodium sulfate, the solvent was distilled off, and the residue was subjected to chromatography on silica gel using toluene–ethyl acetate (6:1) as eluent. Oily substance, yield 0.15 g (35%). UV spectrum: $\lambda_{max}$ 221 nm (ε = 6290). IR spectrum (film), ν, $cm^{-1}$: 3490, 1750, 1700, 1640, 1260, 1240. $^1$H NMR spectrum, δ, ppm: 0.86 s (3H, 18-Me), 1.18 m (12H, 19-Me, 21-Me, CH**Me**$_2$), 2.05 s (6H, OCOMe), 2.70 m (1H, C**H**Me$_2$), 2.84 m (2H, 4'-H), 4.50 t (1H, 5'-H, $J$ = 10 Hz), 5.35 m (1H, 2α-H), 5.47 m (1H, 3α-H), 5.90 br.s (1H, 4-H). Mass spectrum, *m/z*: 544 $[M + 1]^+$, 431 [$M$ – dihydroisoxazole]$^+$, 413 [$M$ – $H_2O$ – dihydroisoxazole]$^+$, 371 [$M$ – AcOH – dihydroisoxazole]$^+$, 328 (100%) [$M$ – AcOH – side chain]$^+$, 311 [$M$ – 2AcOH – dihydroisoxazole]$^+$. Calculated: [$M$ – dihydroisoxazole]$^+$ 431.2434. $C_{25}H_{35}O_6$. Found: ($M$ – dihydroisoxazole) 431.2431

**(20ξ)-2β,3β-Diacetoxy-7α-bromo-20-hydroxy-20-(3-isopropyl-5-isoxazolyl)pregnan-6-one (XI).** Compound **VIII**, 0.1 g (0.19 mmol), was dissolved in 5 ml of glacial acetic acid, and 0.3 ml of 40% hydrobromic acid and a catalytic amount of zinc bromide were added. The mixture was stirred for 2 h at 70–80°C, poured into water, and extracted with ethyl acetate, the extract was dried over sodium sulfate and evaporated, and the residue was subjected to chromatography on silica gel using toluene–ethyl acetate (9:1) as eluent. Oily substance, yield 0.035 g (36%); compound **XI** was isolated as a mixture of two diastereoisomers at a ratio of ~5:2 (according to the $^1$H NMR data). IR spectrum (film), ν, $cm^{-1}$: 1755, 1730, 1250, 1260. $^1$H NMR spectrum, δ, ppm: 0.70 s and 0.76 s (3H, 18-Me), 0.88 s and 0.96 s (3H, 19-Me), 1.22 d and 1.28 d (3H, 21-Me, $J$ = 7 Hz), 1.24 d (6H, CH**Me**$_2$, $J$ = 7 Hz), 2.00 s and 2.06 s (6H, OCOMe), 2.06 s and 2.08 s (3H, OCOMe), 2.82 m (1H, 20-H), 2.91 m (1H, C**H**Me$_2$), 3.34 m (1H, 5α-H), 4.16 d (1H, 7β-H, $J$ = 3 Hz), 4.84 m (1H, 2α-H), 5.26 m (1H, 3α-H), 5.79 s and 5.82 s (1H, 4'-H).

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