PREPARATION OF SOME AMIDIC 6-KETOSTEROIDS AS POTENTIAL INHIBITORS OF POSTECDYSIAL CUTICLE SCLEROTIZATION IN *Pyrrhocoris apterus* L.*

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Compounds *IX*, *XIII* and *XV* were synthesized from dehydroepiandrosterone (*I*). The compound *XV* showed medium activity in inhibiting postecdysial cuticle sclerotization of *Pyrrhocoris apterus* larvae.

In the extention of our work on steroids inhibiting postecdysial cuticle sclerotization in *Pyrrhocoris apterus* (for leading references *cf.*[1]) we became interested in 3- or 2,3--hydroxylated 6-ketosteroids containing an amidic group in the side chain. Compounds *IX*, *XIII* and *XV* were synthesized as suitable models of this type. In the synthesis of these compounds, we set out from dehydroepiandrosterone (*I*) which was subjected to Leuckart reaction following a reported procedure[2,3]. Contrary to the above authors, who prepared the corresponding 3-hydroxy derivative, we obtained the diformyl derivative *II*. This discrepancy was explained by our finding that the reaction yielded the diformyl derivative *II* when a Hershberg stirrer (constantan wire) was used; in experiments with a glass stirrer N-formyl-3-hydroxy derivative was obtained in agreement with the work of the Japanese[2] and Czech[3] authors. The amide *II* was converted to the N-methylamino derivative *III* by lithium aluminum hydride reduction in tetrahydrofuran. Acylation of the amine *III* with isocaproyl chloride was performed in pyridine and led to the O,N-diacyl derivative *IV* without difficulty. Standard procedures were also applied to the subsequent steps, *i.e.* selective hydrolysis of the ester function in the ester amide *IV*, conversion of the hydroxy derivative *V* to the corresponding *p*-toluenesulfonate *VI* and the solvolysis of the latter to provide the 3,5-cyclosteroid *VII*. The secondary hydroxyl group in the compound *VII* was oxidized with chromium trioxide–pyridine complex and the ketone *VIII* thus obtained was used in the preparation of the 3β-hydroxy-6-ketone *IX*, which is one of the required products. Opening of the cyclopropane ring in *VIII* with 6M-H_2SO_4 in acetic acid medium[4] provided a mixture of the 3β-hydroxy steroid *IX* with its acetyl derivative; the latter was saponified by treating the mixture with methanolic potassium hydroxide.

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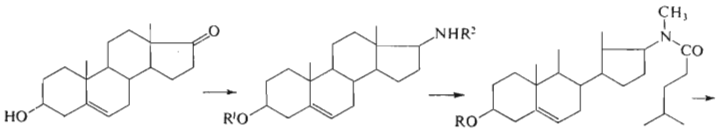
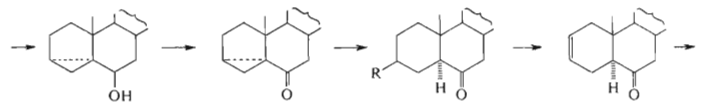
For the preparation of 2,3-dihydroxy derivatives, the cyclopropane ring in *VIII* was first opened with 48% hydrobromic acid following the standard procedure[4]. The reaction resulted in the formation of the 3β-bromo derivative *X* which afforded the 2,3-unsaturated compound *XI* on treatment with lithium bromide in dimethylformamide.

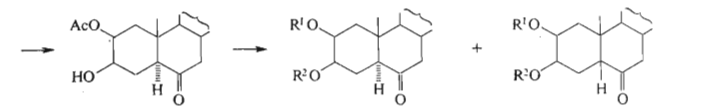


I *II*; $R^1 = R^2 = CHO$ *IV*; $R = C_5H_{11}CO$
III; $R^1 = H$, $R^2 = CH_3$ *V*; $R = H$
VI; $R = Ts$

The unsaturated steroid *XI* was converted to the monoacetate *XII* by treatment with silver acetate and iodine in aqueous acetic acid[5]. In the subsequent step, the 2β-acetoxy group was saponified with potassium carbonate in methanol; as expected, this procedure led to partial isomerization at $C_{(5)}$ to give a mixture of both 2β,3β-diols of the 5α- and 5β-series which were separated by column chromatography on silica gel. The less polar fraction yielded the 5α-diol *XIII* by crystallization. The more polar fraction resisted the attempts at crystallization but the crystalline 5β-diol *XV* could be obtained when the more polar fraction was converted to the readily crystal-



VII *VIII* *IX*, R = OH *XI*
X, R = Br



XII *XIII*; $R^1 = R^2 = H$ *XV*; $R^1 = R^2 = H$
XIV; $R^1—R^2 = C(CH_3)_2$ *XVI*; $R^1—R^2 = C(CH_3)_2$

lizing isopropylidene derivative *XVI* and the latter hydrolyzed with hydrochloric acid in methanol. The assignment of configurations at $C_{(5)}$ in the 6-keto derivatives *XIII* and *XV* is based on values of the molecular amplitudes of the ORD-curves since the 5β-isomeric 6-ketones are known[6] to exert larger negative values than the 5α-isomers.

Of the compounds *IX*, *XIII* and *XV*, only *XV* showed medium activity[1] in inhibiting postecdysial cuticle sclerotization of *Pyrrhocoris apterus* larvae.

EXPERIMENTAL

Melting points are determined on a Kofler block and are uncorrected. Unless stated otherwise, optical rotations are measured in chloroform. The infrared spectra were measured on a Zeiss UR 10 spectrophotometer, ultraviolet spectra on a CF 4 (Optical Milano) spectrophotometer and ORD measurements on a JASCO model ORD/UV-5 spectropolarimeter. The statement "worked up as usual" means: "the solution was washed with water, 5% hydrochloric acid, water, 5% potassium hydrogen carbonate, water, dried with magnesium sulfate and the solvent evaporated at 20—25°C *in vacuo*".

17β-Formylamino-3β-formyloxy-5-androstene (*II*)

A mixture of dehydroepiandrosterone (*I*; 12·8 g; 44·4 mmol), formamide (55 ml) and formic acid (30 ml, 98%) was heated at 175°C for 5·5 hours with stirring. Stirring was continued, the mixture cooled and water (200 ml) was then added. The precipitated product was then separated by filtration, dried (13·8 g) and dissolved in chloroform. The solution was then passed through a layer of sodium sulfate and the solvent evaporated. Repeated crystallization of the residue (9·5 g, 62%, m.p. 246—250°C) from ethanol raised the m.p. to 251—252°C, $[\alpha]_D^{22}$ —112° (*c* 1·38). IR-spectrum (chloroform): 3430, 3395, 1720, 1689, 1506, 1195, 1180 cm^{-1}. For $C_{21}H_{31}NO_3$ (345·5) calculated: 73·05% C, 9·04% H, 4·05% N; found: 73·28% C, 9·13% H, 4·02% N.

3β-Hydroxy-17β-methylamino-5-androstene (*III*)

To a boiling, stirred suspension of lithium aluminum hydride (4 g) in tetrahydrofuran (100 ml) was added dropwise a solution of *II* (1 g, 2·9 mmol) in tetrahydrofuran (150 ml); the mixture was refluxed with continued stirring for 7 hours, cooled and decomposed with aqueous potassium hydroxide (10%; 50 ml). The organic layer was dried with magnesium sulfate, the solvent removed *in vacuo* and the residue crystallized from acetone to yield the product *III* (0·58 g), m.p. 205—210°C, after recrystallization from acetone–6% methanol m.p. 210·5—212·5°C, $[\alpha]_D^{23}$ —54° (*c* 1·3). Literature[7] reports m.p. 206—208°C, $[\alpha]_D^{20}$ —67° (*c* 1·0) and[8] 213—214°C, $[\alpha]_D^{26}$ —51°. IR-spectrum (tetrachloromethane): 3621, 2790, 1061 cm^{-1}. For $C_{20}H_{33}NO$ (303·5) calculated: 79·15% C, 10·96% H, 4·61% N; found: 79·18% C, 10·98% H, 4·41% N.

3β-Isocaproyloxy-17β-(N-methyl-N-isocaproyl)-5-androstene (*IV*)

To a solution of *III* (3·25 g, 10·7 mmol) in pyridine (150 ml) isocaproyl chloride (5·8 g, 43 mmol) was added dropwise and the mixture was refluxed for 5·5 hours. After cooling the reaction mixture was poured into ice water (800 ml), the product taken up in ether and worked up as usual. The residue was crystallized from methanol to give the product *IV* (4·0 g, 75%) m.p. 160—163°C, after recrystallization from methanol m.p. 162—163°C, $[\alpha]_D^{23}$ —92°C (*c* 1·16). IR spectrum (chloroform): 1721, 1713, 1623, 1188 cm^{-1}. For $C_{32}H_{53}NO_3$ (499·7) calculated: 76·91% C, 10·69% H, 2·80% N; found: 77·03% C, 10·87% H, 2·77% N.

17β-(N-Methyl-N-isocaproyl)-5-androsten-3β-ol (*V*)

A solution of *IV*; (7 g, 14 mmol) and potassium hydroxide (3·5 g) in methanol (1 400 ml) was allowed to stand at room temperature for 20 hours. Standard working up and crystallization of the product from acetone yielded the compound *V* (4·0 g, 71%), m.p. 167—169°C, $[\alpha]_D^{23}$ —124° (*c* 1·56). IR-spectrum (chloroform): 3600, 1624 cm^{-1}. For $C_{26}H_{43}NO_2$ (401·6) calculated: 77·75% C, 10·79% H, 3·48% N; found: 77·73% C, 10·80% H, 3·53% N.

17β-(N-Methyl-N-isocaproyl)-3β-*p*-toluenesulfonyloxy-5-androstene (*VI*)

A solution of *V* (6·8 g, 17 mmol) in pyridine (110 ml) was treated with *p*-toluenesulfonyl chloride (7 g) at 32°C overnight, poured into ice-water (600 ml), the precipitate filtered off, dissolved in chloroform and the solution worked up as usual. The product *VI* (9·4 g) was used without further purification in the following step. For characterization, a sample was crystallized at 30°C from acetone–water in the presence of a drop of pyridine to give an analytical sample of *VI*, m.p. 182—186°C, $[\alpha]_D^{22}$ —103° (*c* 1·17). IR-spectrum (chloroform): 1626, 1355, 1176 cm^{-1}. For $C_{33}H_{50}NO_4S$ (556·8) calculated: 71·18% C, 9·05% H, 2·51% N, 5·76% S; found: 71·54% C, 8·97% H, 2·69% N, 5·87% S.

17β-(N-Methyl-N-isocaproyl)-3α,5-cyclo-5α-androstan-6β-ol (*VII*)

The tosylate *VI* (9 g, 16·1 mmol) in acetone (600 ml), potassium acetate (20 g) and potassium hydrogen carbonate (1 g) in water (70 ml) was heated at reflux temperature for 9 hours. After standing at room temperature for an additional 13 hours, most of the acetone was evaporated under reduced pressure, the mixture diluted with water and the product extracted with chloroform. After washing with water, drying with magnesium sulfate and removing the solvent *in vacuo*, the product was purified by column chromatography on silica gel in chloroform solution. The isolated product *VII* (4·8 g, 71·5%), $[\alpha]_D$ —20° (*c* 1·28) was amorphous, but was found to be pure by thin-layer chromatography and the following analytical data: IR-spectrum (chloroform): 3600, 3055, 1627, 1020 cm^{-1}. For $C_{26}H_{43}NO_2$ (401·6) calculated: 77·75% C, 10·79% H, 3·48% N; found: 77·15% C, 10·81% H, 3·41% N.

17β-(N-Methyl-N-isocaproyl)-3α,5-cyclo-5α-androstan-6-one (*VIII*)

The 6β-hydroxy derivative *VII* (3·8 g, 9·45 mmol) was oxidized with pyridine (250 ml)–chromium trioxide (3 g, 30 mmol) complex at 0°C, then at room temperature for 22 hours. Then sodium hydrogen carbonate (3 g), saturated aqueous solution of sodium hydrogen carbonate (200 ml) and water (200 ml) were added in succession. The product was extracted with ether and worked up as usual. The oily residue (3·8 g) was diluted with light petroleum (40 ml) to yield 2·5 g of compound *VIII*, m.p. 108—115°C. Recrystallization from hexane raised the m.p. to 115—119°C, $[\alpha]_D^{23}$ —34° (*c* 1·32). IR-spectrum (chloroform): 3080, 1680, 1628 cm^{-1}. For $C_{26}H_{41}NO_2$ (399·6) calculated: 78·14% C, 10·34% H, 3·51% N; found: 78·37% C, 10·40% H, 3·38% N.

3β-Hydroxy-17β-(N-methyl-N-isocaproyl)-5α-androstan-6-one (*IX*)

The ketone *VIII* (0·5 g, 1·25 mmol) was treated with 6M-H_2SO_4 (1·5 ml) in acetic acid (11 ml) solution at 35°C for 45 hours. The mixture was then poured into ice water (80 ml) and the product taken up in ether. The ethereal layer was washed with water, saturated solution of sodium hydrogen carbonate, water and dried with magnesium sulfate. The solvent was evaporated under reduced pressure and the residue (0·6 g) was dissolved in methanol (15 ml), potassium hydroxide (0·28 g)

in water (1 ml) was added and the mixture let stand for 2 hours at room temperature. The solvent was then evaporated, the residue diluted with water, the precipitate filtered off and crystallized from acetone to give 0·39 g (75·6%) of the product *IX*, m.p. 205—208°C, $[\alpha]_D^{24}$ −90° (*c* 1·25). IR-spectrum (chloroform): 3 600, 1 709, 1 629 cm^{-1}. For $C_{26}H_{43}NO_3$ (417·6) calculated: 74·77% C, 10·38% H, 3·35% N; found: 75·02% C, 10·57% H, 3·20% N.

3β-Bromo-17β-(N-methyl-N-isocaproyl)-5α-androstan-6-one (*X*)

To a stirred solution of the ketone *VIII* (1·51 g, 3·78 mmol) in acetic acid (10 ml) hydrobromic acid (48%, 15 ml) was added. After standing at room temperature for 19 hours, the product was precipitated by pouring the mixture into water (100 ml), filtered off and dissolved in chloroform. Washing with potassium hydrogen carbonate and water, drying with magnesium sulfate, evaporating the solvent and crystallization of the residue (1·7 g) from acetone provided the product *X* (1·1 g, 62%), m.p. 185—189°C. Recrystallization of a sample from acetone–light petroleum gave the substance, m.p. 187—189°C, $[\alpha]_D^{23}$ −71° (*c* 1·3). IR-spectrum (chloroform): 1 710, 1 629 cm^{-1}. For $C_{26}H_{42}BrNO_2$ (480·5) calculated: 64·98% C, 8·81% H, 16·63% Br, 2·91% N; found: 64·38% C, 8·87% H, 16·61% Br, 2·63% N.

17β-(N-Methyl-N-isocaproyl)-5α-androst-2-en-6-one (*XI*)

A mixture of the bromo derivative *X* (1 g, 2·08 mmol), lithium carbonate (1·2 g) and lithium bromide (0·5 g) in dimethylformamide (25 ml) was heated at reflux temperature for 2 hours. The mixture was cooled, diluted with benzene (75 ml), filtered free of inorganic salts, diluted with light petroleum (75 ml), washed with water and dried with magnesium sulfate. After evaporating the solvent, the residue (0·75 g) was crystallized from acetone to give the product *XI* (0·4 g, 50%), m.p. 163—171°C, $[\alpha]_D^{23}$ −61° (*c* 1·25). IR-spectrum (chloroform): 1 704, 1 628 cm^{-1}. For $C_{26}H_{41}NO_2$ (399·6) calculated: 78·14% C, 10·34% H, 3·51% N; found: 78·54% C, 10·24% H, 3·48% N.

2β-Acetoxy-3β-hydroxy-17β-(N-methyl-N-isocaproyl)-5α-androstan-6-one (*XII*)

The compound *XI* (200 mg, 0·5 mmol) was dissolved in acetic acid (15 ml) and the following was added in succession: water (0·35 ml), silver acetate (310 mg) and, in the course of five minutes, finely divided iodine (200 mg). The mixture was stirred and heated at 50—60°C for 3 hours, cooled and filtered through a layer of sodium chloride. The solvent was removed under reduced pressure, the residue dissolved in ethyl acetate (50 ml), the solution successively washed with water, 5% solution of potassium hydrogen carbonate, 3% solution of sodium thiosulfate, water and dried with sodium sulfate. Evaporating the solvent under reduced pressure and crystallization from ethyl acetate–light petroleum furnished the product *XII* (186 mg, 78%), m.p. 225—240°C. Further crystallization from ethyl acetate raised the m.p. to 225—235°C, $[\alpha]_D^{23}$ −62°, (*c* 0·88). IR-spectrum (chloroform): 3 585, 1 725, 1 708, 1 625, 1 250, 1 070 cm^{-1}. For $C_{28}H_{45}NO_5$ (475·6) calculated: 70·69% C, 9·53% H, 2·94% N; found: 70·88% C, 9·55% H, 3·00% N.

2β,3β-Isopropylidenedioxy-17β-(N-methyl-N-isocaproyl)-5α-androstan-6-one (*XIV*)

A solution of potassium hydrogen carbonate (300 mg) in water (6 ml) was added to the acetoxy derivative *XII* (287 mg, 0·6 mmol) in methanol and the mixture was refluxed for 30 minutes. The solvent was then evaporated under reduced pressure and the residue was diluted with water (80 ml). The content of the flask was neutralized with diluted hydrochloric acid, the organic

material extracted with ethyl acetate, the solution washed with water and dried with magnesium sulfate. The solvent was then evaporated and the residue (280 mg) subjected to subsequent reaction without purification. It was dissolved in acetone (25 ml) and treated[9] with a 1% solution of phosphomolybdenic acid in acetone (20 ml) at room temperature. After standing one hour, 25% ammonia (25 ml) and water (50 ml) were added in succession. The precipitate was taken up in ether, the solution washed with water and dried with magnesium sulfate. Evaporating the solvent and repeated crystallization from acetone gave the acetonide *XIV* (80 mg), m.p. 212 to 215°C, $[\alpha]_D^{20}$ −61° (*c* 0·97). IR-spectrum (chloroform): 1707, 1627, 1246, 1050 cm^{-1}. ORD (chloroform, 24°C): $[\Phi]_{260}$ +6050°, $[\Phi]_{272}$ +6640°, $[\Phi]_{292}$ ±0°, $[\Phi]_{300}$ −5130°, $[\Phi]_{304}$ −6970° (inflex), $[\Phi]_{312}$ −8750°, $[\Phi]_{320}$ −6320°, $[\Phi]_{340}$ −2900°, $[\Phi]_{400}$ −1050°; $a = -154$. For $C_{29}H_{47}NO_4$ (473·7) calculated: 73·53% C, 10·00% H, 2·96% N; found: 73·89% C, 10·15% H, 3·08% N.

2β,3β-Dihydroxy-17β-(N-methyl-N-isocaproyl)-5α-androstan-6-one (*XIII*)

a) 10% Hydrochloric acid was added[6] to a solution of the acetonide *XIV* (165 mg, 0·349 mmol) in methanol (55 ml), the mixture set aside for one hour at room temperature, the solvent removed under reduced pressure, the residue diluted with water (50 ml) and the product taken up in ether. The solution was washed with water and dried with magnesium sulfate. Evaporating the solvent under reduced pressure and crystallization of the residue (147 mg) from ethyl acetate gave the diol *XIII* (88 mg, 58%), m.p. 222—225°C, $[\alpha]_D^{21}$ −78° (*c* 0·87). IR-spectrum (chloroform): 3600, 1707, 1624, 1060 cm^{-1}. ORD (chloroform 24°C): $[\Phi]_{260}$ +3230°, $[\Phi]_{273}$ +3700°, $[\Phi]_{285}$ +2080°, $[\Phi]_{291}$ ±0°, $[\Phi]_{302}$ −4970°, $[\Phi]_{305}$ −5200°, $[\Phi]_{311}$ −6360°, $[\Phi]_{325}$ −3470°, $[\Phi]_{360}$ −1620°, $[\Phi]_{400}$ −810°; $a = -100{\cdot}6$. For $C_{26}H_{43}NO_4$ (433·6) calculated: 72·01% C, 10·00% H, 3·23% N; found: 72·11% C, 9·88% H, 3·08% N.

b) A solution of potassium carbonate (260 mg) in water (2 ml) was added to the acetyl derivative *XII* (261 mg, 0·548 mmol) in methanol (25 ml) and allowed to stand at 35°C for 23 hours. The solution was concentrated under reduced pressure, the residue diluted with water, dilute hydrochloric acid added until neutral reaction and the product isolated with ethyl acetate. Washing with water, drying with magnesium sulfate and evaporating left a residue (250 mg) which was chromatographed on silica gel in chloroform solution. Crystallization of the less polar fraction from ethyl acetate gave the 5α-diol *XIII*. The more polar fraction (40 mg) contained mainly 5β-diol but resisted all attempts at crystallization.

2β,3β-Isopropylidenedioxy-17β-(N-methyl-N-isocaproyl)-5β-androstan-6-one (*XVI*)

The more polar diol (65 mg), obtained by hydrolysis of the acetyl derivative *XII* according to procedure *b*), was dissolved in acetone (10 ml) and treated[9] with a 1% solution of phosphomolybdenic acid in acetone (8 ml) for 90 minutes at room temperature. After successive addition of 25% aqueous ammonia (5 ml) and water (20 ml) the product was taken up in ether, the extract washed with water, dried with magnesium sulfate, the solvent removed under reduced pressure and the residue (45 mg) crystallized from methanol–water. Recrystallization gave the 5β-acetonide *XVI* (25 mg), m.p. 177—183°C, $[\alpha]_D^{22}$ −92° (*c* 0·86). IR-spectrum (chloroform): 1702, 1629, 1247, 1054, 1035 cm^{-1}. ORD (chloroform, 24°C): $[\Phi]_{260}$ +6990°, $[\Phi]_{275}$ +8080°, $[\Phi]_{296}$ ±0°, $[\Phi]_{308}$ −8230°, $[\Phi]_{317}$ −9780°, $[\Phi]_{335}$ −4810°, $[\Phi]_{350}$ −3100°, $[\Phi]_{400}$ −1240°; $a = -179$. For $C_{29}H_{47}NO_4$ (473·7) calculated: 73·53% C, 10·00% H, 2·96% N; found: 73·56% C, 10·16% H, 2·91% N.

2β,3β-Dihydroxy-17β-(N-methyl-N-isocaproyl)-5β-androstan-6-one (*XV*)

The 5β-acetonide *XVI* (30 mg) in methanol (10 ml) was treated[6] with 10% hydrochloric acid (0·4 ml) for 1 hour at room temperature. The solution was concentrated under reduced pressure, water (25 ml) was added and the product extracted with ether. The solution washed with water, dried with magnesium sulfate, the solvent removed under reduced pressure and the residue (17 mg) crystallized from ethyl acetate–light petroleum, to yield the 5β-diol *XV* (10 mg), m.p. 167—170°C. IR-spectrum (chloroform): 3600, 3560—3400, 1051, 1700, 1624 cm^{-1}. ORD (chloroform, 24°C): $[\Phi]_{260}$ +2610°, $[\Phi]_{275}$ +7390°, $[\Phi]_{285}$ +5670°, $[\Phi]_{289}$ ±0°, $[\Phi]_{300}$ −3850°, $[\Phi]_{309}$ −9315° (inflex), $[\Phi]_{317}$ −10490°, $[\Phi]_{325}$ −8030°, $[\Phi]_{350}$ −3530° $[\Phi]_{400}$ −1820°; $a = -178{\cdot}8$. For $C_{26}H_{43}NO_4$ (433·6) calculated: 72·01% C, 10·00% H, 3·23% N; found: 71·94% C, 10·00% H, 3·10% N.

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