SYNTHESIS OF 14-DEOXY-14α-STROPHANTHIDIN

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A seventeen step synthesis of 3β,5-dihydroxy-19-oxo-5β,14α-card-20(22)-enolide (*II*, title compound) from 3β-benzoyloxy-5-pregnen-20-one (*IV*) is described. Characteristic features of this approach are the protection of the 19-hydroxy group as methyl ether, recovery of the hydroxyl and the introduction of 5β-hydroxyl on the basis of neighboring group participation. The 19-hydroxy group was regenerated in *XIV* by a two-step process: Addition of hypobromous acid to the 5,6-double bond leads to the 5α,6α-bromonium ion *XV*, which is cleaved with $5(O)^n$ participation of the 19-methoxyl group to the cyclic ether *XVI*, the latter being converted to the 19-hydroxy derivative *XVII* by treatment with zinc and acetic acid. The 5β-hydroxy group was introduced by hypobromous acid addition to the 5,6-unsaturated 19-formate *XVIII* which proceeds with $6(O)^{\pi,n}$ participation of the formate group (*XVIII* → *XIX* → *XX*).

In the continuation of our work pursuing the goal of finding simpler partial synthetic routes to steroid cardiotonics, we turned our attention to the model experiments on the synthesis of strophanthidin (*I*). The aim of the present paper was to find a synthetic route for the construction of the substituted A/B-ring part of strophanthidin (*I*) allowing, at the same time, synthesis of the side chain lactone ring. In this paper we describe the synthesis of the model compound *II* containing all these structural features. It differs from strophanthidin (*I*) by lacking the 14β-hydroxyl group and by *trans*-junction of the rings C and D.

In our synthesis, pregnenolone benzoate (*IV*) was used as a starting material. The choice of methods for the stepwise construction of the polyfunctional aglycone molecule led logically to an intermediate of the type *III* in which selective protection of three hydroxyl groups in positions 3, 19 and 21 was a crucial problem.

The character of the ester group in the side chain is determined by the choice of acetoxylation as the method used for functionalization at $C_{(21)}$. For the protection of 3β-hydroxyl benzoylation appears convenient and the 19-hydroxyl may be well protected as a methoxyl group. The latter protection may appear rather unusual, but we have shown earlier that in this case the hydroxyl group can be easily recovered[1-6]. Another possibility of protecting the 19-hydroxyl by the formation of the

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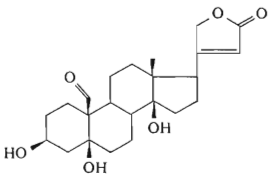
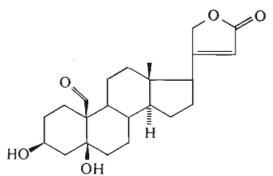
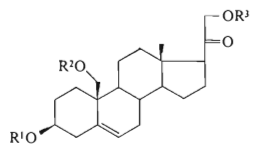
5α-bromo-6β,19-epoxy grouping was used recently in our synthesis of the related model compound, 14-deoxy-14α-strophanthidol[7].



I



I₁

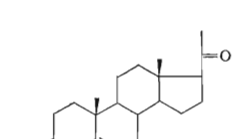


III

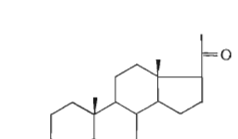
Addition of hypobromous acid (generated *in situ* from N-bromoacetamide and aqueous perchloric acid) in dioxane to the pregnenolone benzoate (*IV*) led to the diaxial bromohydrin *V* which on usual reaction with lead tetraacetate was cyclized to the 6β,19-epoxy derivative *VI*. Reduction of the latter with zinc dust in hot acetic acid smoothly afforded the 19-alcohol *VII* which was methylated using sodium hydride and methyl iodide to give the methyl ether *VIII*. The latter compound was also obtained from the known[8] dimethoxy derivative *XIII via* 3β-alcohol *IX* and subsequent benzoylation. The methyl ether *VIII* was acetoxylated in excellent yield with lead tetraacetate in the presence of boron trifluoride etherate to give the 21-acetoxy derivative *X*. The acetoxy group in the latter compound was selectively hydrolyzed under acidic conditions to the 21-alcohol *XI*. The 21-alcohol *XI* was esterified with diethylphosphonoacetic acid in the presence of N,N'-dicyclohexylcarbodiimide and the resulting ester *XII* was cyclized with potassium tert-butoxide to yield the unsaturated lactone *XIV*.

The hydroxyl group at position 19 was recovered by a two step procedure: Addition of hypobromous acid to the 5,6-double bond afforded in high yield the bromo epoxide *XVI*, which upon reduction with zinc in acetic acid smoothly gave the 19-alcohol *XVII*. The addition proceeds *via* the bromonium ion *XV* which is opened with $5(O)^n$ participation by an attack of the 19-methoxyl group (for notation *cf.* ref.[4]). It is pertinent to note that we observed the easy and extremely mild recovery of unsaturated alcohols from the corresponding methyl ethers also in other cases[1-6].

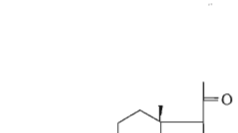
We believe that this procedure is likely to become a general method for protection of unsaturated alcohols, provided the steric arrangement[6] enables the $5(O)^n$ participation.



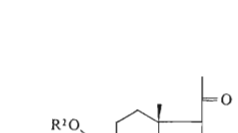
IV



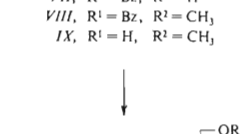
V



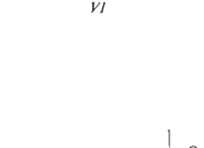
VI



VII, $R^1 = Bz$, $R^2 = H$
VIII, $R^1 = Bz$, $R^2 = CH_3$
IX, $R^1 = H$, $R^2 = CH_3$



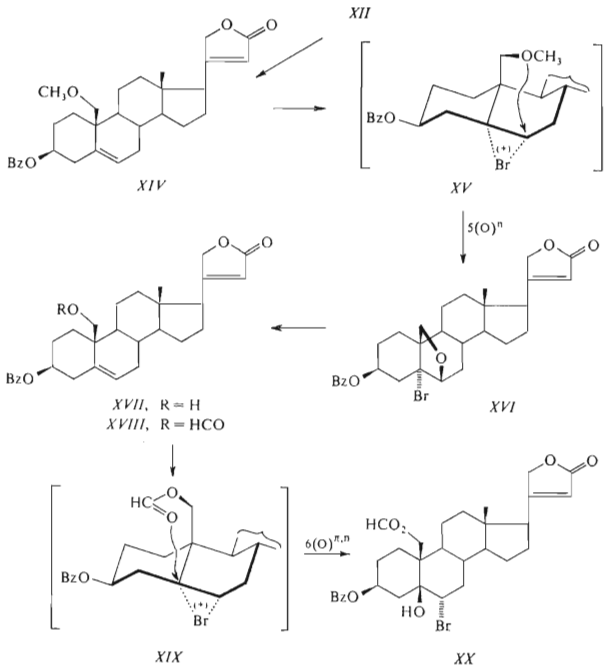
X, R = Ac
XI, R = H
XII, $R = OC-CH_2-P(O)(OC_2H_5)_2$



XIII

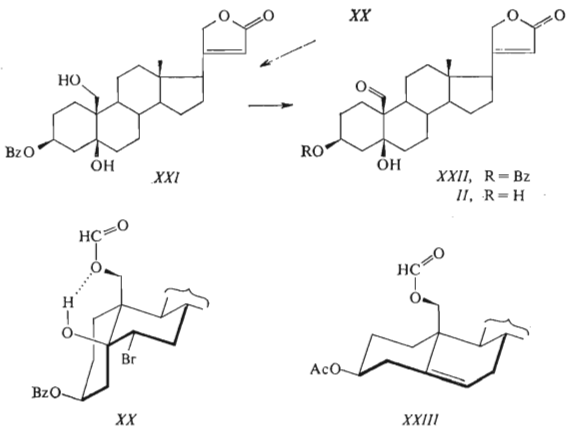
The known[9-12] methods for introduction of the 5β-hydroxy group based on hydride reduction or hydrogenation of the 5β,6β-epoxides and reduction of 4β,5β-epoxides with chromous salts give a low yield of the desired product. In the present paper

we used a method which we recently developed[4,7,13]: Addition of hypobromous acid to the formate *XVIII* proceeds with 6(O)$^{\pi,n}$ participation of the carbonyl oxygen in cleavage of the intermediary bromonium ion *XIX* to give the diequatorial bromohydrin *XX* in 67% yield. The subsequent treatment of the bromohydrin with Raney-Ni removed both the bromine atom and the formate group to give the diol *XXI* in a single step. One fact about this reaction should be emphasized: When an analogous compound, 5-cholesten-3β,19-diol 3-acetate 19-formate (*XXIII*) lacking the 5β-hydroxyl is treated with Raney-Ni under the same conditions, the formate group is removed about ten times slower. We explain this behavior by the accelerating influence of the neighboring 5β-hydroxyl[11,14,15].



Oxidation of 19-alcohol *XXI* with Jones' reagent furnished the 19-aldehyde *XXII* in which the benzoyloxy group was smoothly saponified with potassium hydrogen

carbonate to afford the target compound *II*, a deoxy-analog of strophanthidin (*I*). This rapid hydrolysis is of interest, since, generally, the axial benzoyloxy group is relatively stable under these conditions. Again, this fact may be explained by the intervention of the 5β-hydroxy group.



The present synthesis shows that the construction of the A/B-ring part of strophanthidin allowing at the same time synthesis of the side chain lactone ring can be conducted in a relatively simple way. The first and to date only synthesis of strophanthidin was published by Japanese authors[12] while our work was in progress. The approach of the Japanese group was different and the introduction of the 5β--hydroxyl was more complicated. We believe that our approach is a promising route to the synthesis of strophanthidin.

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried at 50°C/26 Pa (0·2 Torr). Optical measurements were carried out in chloroform with an error of ±3°. The infrared spectra were recorded on a Zeiss UR 20 spectrometer in tetrachloromethane unless otherwise stated. The ^{1}H-NMR spectra were recorded on a Tesla BS 476 instrument (60 MHz) in deuteriochloroform at 30°C with tetramethylsilane as internal reference. Chemical shifts are given in ppm. Apparent coupling constants were obtained from the first order analysis. The CD spectra were recorded on a Dichrographe II (Jouan-Roussel) in dioxane. The mass spectra were recorded on a Jeol JMS D-100 spectrometer operating at 75 eV. The samples were introduced using a direct inlet at 140°C. The elemental compositions of the ions were determined by ac-

curate mass measurements. The identity of the samples prepared by different routes was checked by mixture melting point determination, by thin-layer chromatography (TLC) and by infrared and ^{1}H-NMR spectra. Usual work up of an ethereal solution means washing the solution with 5% aqueous hydrochloric acid, water, a 5% aqueous potassium hydrogen carbonate solution, water, drying with sodium sulfate and evaporation of the solvent *in vacuo*.

3β,5-Dihydroxy-19-oxo-5β,14α-card-20(22)-enolide (*II*)

The benzoate *XXII* (35 mg) was dissolved in methanol (5 ml) and refluxed with potassium hydrogen carbonate (50 mg) in water (0·5 ml) for 30 min. The solvent was evaporated, the residue was treated with ether, chloroform and water, the organic layer was washed with water, dried and evaporated. The residue was chromatographed on one preparative silica gel plate (20 × 10 cm) using double development with a mixture of benzene, ether and acetone (80 : 10 : 10). Corresponding zone was collected, eluted with a mixture of benzene and ether and the eluent was evaporated to yield the foam of the diol *II* (23 mg). $[\alpha]_D^{20}$ +22° (*c* 2·0). IR spectrum: 1629, 1748, 1785, 2761, 3475, 3610 cm^{-1}. For $C_{23}H_{32}O_5$ (388·5) calculated: 71·11% C, 8·30% H; found: 70·94% C, 8·18% H.

3β-Benzoyloxy-5-bromo-6β-hydroxy-5α-pregnan-20-one (*V*)

The benzoate *IV* (10 g) was dissolved in dioxane (400 ml), a solution of 70% perchloric acid (3 ml) in water (20 ml) was added and the solution was treated for 1 h with N-bromoacetamide (4 g) at room temperature. The mixture was diluted dropwise with water (300 ml) and set aside for 2 h. The crude product was collected by suction, washed with water, air-dried and recrystallized from a mixture of chloroform and light petroleum to yield the bromohydrin *V* (8·2 g). m.p. 185—186°C, $[\alpha]_D^{20}$ +14° (*c* 2·6). ^{1}H-NMR spectrum: 0·63 (3 H, s, 18-H), 1·36 (3 H, s, 19-H), 2·08 (3 H, s, 21-H), 4·22 (1 H, m, W = 12 Hz, 6α-H), 5·70 (1 H, m, W = 30 Hz, 3α-H). For $C_{28}H_{37}BrO_4$ (517·5) calculated: 64·99% C, 7·21% H, 15·44% Br; found: 64·76% C, 7·35% H, 15·71% Br.

3β-Benzoyloxy-5-bromo-6β,19-epoxy-5α-pregnan-20-one (*VI*)

A mixture of lead tetraacetate (6 g) and calcium carbonate (4 g) in benzene (100 ml) was refluxed and stirred for 2 h. A suspension of the bromohydrin *V* (7 g) in benzene (300 ml), then iodine (200 mg) was added and the mixture was refluxed while stirring for 4 h. The inorganic material was separated by filtration, the solution was washed with water, aqueous 5% potassium hydrogen carbonate, an aqueous solution of sodium thiosulphate, water, dried and the solvent evaporated. The residue was crystallized from a mixture of chloroform and methanol to yield *VI* (5·2 g), m.p. 250—251°C, $[\alpha]_D^{20}$ +52° (*c* 1·8). ^{1}H-NMR spectrum: 0·67 (3 H, s, 18-H), 2·10 (3 H, s, 21-H), (1 H, d, J = 9 Hz, 19-H), 4·02 (1 H, d, J = 9 Hz, 19-H), 4·04 (1 H, m, W = 9 Hz, 6α-H), 5·50 (1 H, m, W = 30 Hz, 3α-H). For $C_{28}H_{35}BrO_4$ (515·5) calculated: 65·24% C, 6·84% H, 15·50% Br; found: 65·19% C, 6·72% H, 15·83% Br.

3β-Benzoyloxy-19-hydroxy-5-pregnen-20-one (*VII*)

The bromo epoxide *VI* (5·1) g) was dissolved in a mixture of dioxane (30 ml), acetic acid (30 ml) and methanol (5 ml) and stirred at 90°C with powdered zinc (7 g) for 5 min. The inorganic material was separated by filtration, the hot solution was diluted with water to yield the alcohol *VII*

(3·7 g), m.p. 216—217°C, $[\alpha]_D^{20}$ +52° (*c* 2·2). ^{1}H-NMR spectrum: 0·68 (3 H, s, 18-H), 2·10 (3 H, s, 21-H), 3·45 (2 H, m, 19-H), 4·90 (1 H, m, W = 30 Hz, 3α-H), 5·78 (1 H, m, W = 15 Hz, 6-H). For $C_{28}H_{36}O_4$ (436·6) calculated: 77·03% C, 8·31% H; found: 69·94% C, 8·26% H.

3β-Benzoyloxy-19-methoxy-5-pregnen-20-one (*VIII*)

a) *From 3β-benzoyloxy-19-hydroxy-5-pregnen-20-one* (VII): The alcohol *VII* (3·6 g) was dissolved in a mixture of hexamethylphosphortriamide (10 ml) and benzene (10 ml), methyl iodide (5 ml) and sodium hydride (360 mg) were added and the mixture was stirred at room temperature for 24 h. The mixture was diluted with ether, the excess of sodium hydride was decomposed with water and aqueous 5% hydrochloric acid, and the ethereal layer was worked up as usual. The residue was chromatographed on a silica gel column (100 g). Elution with a mixture of light petroleum and ether (80 : 20) and crystallization from a mixture of acetone, methanol and water yielded *VIII* (0·8 g), m.p. 155—157°C, $[\alpha]_D^{20}$ +33° (*c* 1·9). ^{1}H-NMR spectrum: 0·68 (3 H, s, 18-H), 2·10 (3 H, s, 21-H), 3·30 (3 H, s, CH_3O), 3·32 (1 H, d, J = 10 Hz, 19-H), 3·64 (1 H, d, J = 10 Hz, 19-H), 4·90 (1 H, m, W = 30 Hz, 3α-H), 5·67 (1 H, m, W = 11 Hz, 6-H). For $C_{29}H_{38}O_4$ (450·6) calculated: 77·30% C, 8·50% H; found: 77·17% C, 8·39% H.

b) *From 3β-hydroxy-19-methoxy-5-pregnen-20-one* (IX): The alcohol *IX* (1·3 g) was dissolved in pyridine (5 ml) and treated with benzoyl chloride (1 ml) at room temperature for 3 h. The mixture was decomposed with ice and water, the product was extracted into ether and the ethereal solution was worked up as usual to yield the crude benzoate *VIII* (1·35 g). The sample was crystallized from a mixture of acetone, methanol and water, m.p. 157—158°C.

3β-Hydroxy-19-methoxy-5-pregnen-20-one (*IX*)

The 3,5-cyclo derivative[8] *XIII* (1·4 g) was dissolved in a mixture of acetone (20 ml) and water (3 ml) and after addition of 10% aqueous perchloric acid solution (0·4 ml) the mixture was refluxed for 2 h. The solvent was partially removed *in vacuo*, the residue was treated with ether and water, the ethereal layer was washed with water, a 5% aqueous potassium hydrogen carbonate solution, water, dried and the solvent was evaporated to yield the crude alcohol *IX* (1·3 g). The sample was crystallized from a mixture of acetone and light petroleum to afford the pure *IX*, m.p. 153—154°C, $[\alpha]_D^{20}$ +9° (*c* 1·7). ^{1}H-NMR spectrum: 0·63 (3 H, s, 18-H), 2·07 (3 H, s, 21-H), 3·24 (1 H, d, J = 10 Hz, 19-H), 3·56 (1 H, d, J = 10 Hz, 19-H), 3·25 (3 H, s, CH_2O), 5·56 (1 H, m, W = 15 Hz, 6-H). For $C_{22}H_{34}O_3$ (346·5) calculated: 76·26% C, 9·87% H; found: 76·12% C, 9·84% H.

3β-Benzoyloxy-19-methoxy-21-acetoxy-5-pregnen-20-one (*X*)

To a stirred solution of the ketone *IX* (1·32 g) in benzene (40 ml) a solution of methanol (5·0 ml) in benzene (40 ml), a solution of boron trifluoride etherate (12 ml) in benzene (40 ml) and powdered lead tetraacetate (3·2 g) were added simultaneously in the course of 4 h. The mixture was diluted with ether, water and 5% aqueous hydrochloric acid, and the ethereal layer was worked up as usual. The residue was crystallized from a mixture of acetone, methanol and water to yield the compound *X* (1·3 g), m.p. 134—135°C, $[\alpha]_D^{20}$ +32° (*c* 1·3). ^{1}H-NMR spectrum: 0·68 (3 H, s, 18-H), 2·13 (3 H, s, CH_3CO_2), 3·28 (3 H, s, CH_3O), 3·30 (1 H, d, J = 10 Hz, 19-H), 3·64 (1 H, d, J = 10 Hz, 19-H), 4·44 (1 H, d, J = 16 Hz, 21-H), 4·78 (1 H, d, J = 16 Hz, 21-H), 4·90 (1 H, m, W = 30 Hz, 3α-H), 5·69 (1 H, m, W = 12 Hz, 6-H). For $C_{31}H_{40}O_6$ (508·7) calculated: 73·20% C, 7·93% H; found: 73·07% C, 7·96% H.

3β-Benzoyloxy-21-hydroxy-19-methoxy-5-pregnen-20-one (*XI*)

The acetate *X* (1·3 g) was dissolved in a mixture of chloroform (10 ml) and methanol (50 ml) and treated for 2 days with a solution of 70% perchloric acid (1·5) in water (1·5 ml) at room temperature. The solution was concentrated *in vacuo*, diluted with ether and water, the ethereal layer was washed with water, 5% aqueous potassium hydrogen carbonate, water, dried and the solvent was evaporated. The residue was crystallized from a mixture of acetone and n-heptane to yield *XI* (1·0 g) m.p. 155—156°C, $[\alpha]_D^{20}$ +25° (*c* 1·7). ^{1}H-NMR spectrum: 0·68 (3 H, s, 18-H), 3·30 (3 H, s, CH_3O), 3·29 (1 H, d, J = 10 Hz, 19-H), 3·65 (1 H, d, J = 10 Hz, 19-H), 4·16 (2 H, d, J = 5 Hz, 21-H), 4·90 (1 H, m, W = 30 Hz, 3α-H), 5·65 (1 H, W = 15 Hz, 6-H). For $C_{29}H_{38}O_5$ (466·6) calculated: 74·65% C, 8·21% H; found: 74·38% C, 8·13% H.

3β-Benzoyloxy-19-methoxy-14α-carda-5,20(22)-dienolide (*XIV*)

A solution of the alcohol *XI* (550 mg), diethylphosphonoacetic acid (400 mg) and N,N'-dicyclohexylcarbodiimide (350 mg) in benzene (15 ml) and pyridine (0·1 ml) was stirred at room temperature for 6 h. The N,N'-dicyclohexylurea was separated by suction, washed with benzene and the filtrate was evaporated to yield the crude phosphonate *XII* which was not purified. The crude phosphonate *XII* was dissolved in 1,2-dimethoxyethane (5 ml) and stirred with potassium tert-butylate (200 mg) at 0°C for 1 h. The mixture was acidified with 5% aqueous hydrochloric acid, diluted with ether and water and the organic phase was worked up as usual. The residue was crystallized from a mixture of acetone and n-heptane to yield the lactone *XIV* (420 mg), m.p. 220—222°C, $[\alpha]_D^{20}$ —28° (*c* 1·5). IR spectrum (chloroform): 1278, 1628, 1712, 1749, 1786 cm^{-1}. ^{1}H-NMR spectrum: 0·67 (3 H, s, 18-H), 3·33 (3 H, s, CH_3O), 3·34 (1 H, d, J = 10 Hz, 19-H), 3·69 (1 H, d, J = 10 Hz), 4·75 (1 H, brd s, 21-H), 5·70 (1 H, m, W = 14 Hz, 6-H), 5·85 (1 H, m, W = 5 Hz, 22-H). For $C_{31}H_{38}O_5$ (490·6) calculated: 75·89% C, 7·81% H; found: 75·63% C, 7·74% H.

3β-Benzoyloxy-5-bromo-5β,19-epoxy-5α,14α-card-20(22)-enolide (*XVI*)

The methoxy derivative *XIV* (400 mg) was dissolved in a mixture of dioxane (8 ml) and water (1 ml) and treated with 10% aqueous perchloric acid (0·6 ml) and N-bromoacetamide (160 mg) at room temperature for 1 h. The mixture was diluted with water, the product isolated with suction, dissolved in ether and the ethereal solution was washed with water, a 5% aqueous potassium hydrogen carbonate solution, aqueous sodium thiosulfate solution, water, dried and evaporated. The residue was purified on four preparative silica gel plates using chloroform for development. Corresponding zones were collected and eluted with ether to yield the epoxide *XVI* (350 mg). A sample was crystallized from a mixture of n-heptane and acetone, m.p. 284—285°C, $[\alpha]_D^{20}$ —3° (*c* 2·1), identical with an authentic sample[7].

3β-Benzoyloxy-19-formyloxy-14α-carda-5,20(22)-dienolide (*XVIII*)

The alcohol[7] *XVII* (800 mg) was treated for 5 min with 85% aqueous formic acid (50 ml) at 70°C and set aside for 1 h. The mixture was diluted with water, extracted with ether, the ethereal layer was washed with water, a 5% aqueous potassium hydrogen carbonate solution, water, dried and the solvent was evaporated. The residue was crystallized from aqueous ethanol to give the formate *XVIII* (630 mg), m.p. 215—218°C, $[\alpha]_D^{20}$ —40° (*c* 1·0). ^{1}H-NMR spectrum: 0·67 (3 H, s, 18 H), 4·08 (1 H, d, J = 13 Hz, 19-H), 4·64 (1 H, d, J = 13 Hz, 19-H), 4·76 (2 H, brd s, 21-H), 5·00 1 H, m, W = 30 Hz, 3α-H), 5·70 (1 H, m, W = 16 Hz, 6-H), 5·83 (1 H, m, W = = 7 Hz, 22-H), 8·12 (1 H, s, HCO_2). For $C_{31}H_{36}O_6$ (504·6) calculated: 73·79% C, 7·19% H found: 73·55% C, 7·24% H.

3β-Benzoyloxy-6α-bromo-19-formyloxy-5-hydroxy-5β,14α-card-20(22)-enolide (*XX*)

A solution of the olefin *XVIII* (600 mg) in dioxane (25 ml) and water (1·5 ml) was treated with 10% aqueous perchloric acid (1·2 ml) and N-bromoacetamide (250 mg) at room temperature for 30 min. The mixture was diluted with ether and water, the ethereal layer was washed with water, a 5% aqueous potassium hydrogen carbonate solution, aqueous sodium thiosulfate solution, water, dried and evaporated. The residue was chromatographed on a column of silica gel (30 g) with a mixture of benzene, ether and acetone (94 : 5 : 1). Corresponding fractions were collected and evaporated to yield the crude product. A sample was crystallized from a mixture of acetone and n-heptane to give the compound *XX*, m.p. 148—152°C, $[\alpha]_D^{20}$ +18° (*c* 1·9). ^{1}H-NMR spectrum: 0·62 (3 H, s, 18-H), 4·50 (2 H, s, 19-H), 4·58 (1 H, m, 6β-H, overlapped by signals of other protons), 4·73 (2 H, brd s, 21-H), 5·52 (1 H, m, W = 15 Hz, 3α-H), 5·85 (1 H, m, W = 8 Hz, 22-H), 8·15 (1 H, s, HCO_2). For $C_{31}H_{37}BrO_7$ (601·6) calculated: 61·90% C, 6·20% H, 13·28% Br; found: 61·74% C, 6·11% H, 13·49% Br.

3β-Benzoyloxy-5,19-dihydroxy-5β,14α-card-20(22)-enolide (*XXI*)

The bromohydrin *XX* (450 mg) in ethanol (15 ml) was refluxed while stirring with freshly prepared Raney-nickel (500 mg) for 6 h. The inorganic material was filtered off, the filtrate and washings were evaporated *in vacuo*, the residue was dissolved in ether, the solution washed with water, dried and evaporated. The residue was chromatographed on a column of silica gel (20 g) using a mixture of benzene, ether and acetone (93 : 52) as eluent to yield the crude *XXI* (320 mg).; A sample was crystallized from a mixture of acetone and n-heptane, m.p. 183—185°C, $[\alpha]_D^{20}$ +14° (*c* 3·8). IR spectrum (KBr): 1280, 1702, 1743, 1775, 3220, 3380 cm^{-1}. For $C_{20}H_{38}O_6$ (494·6) calculated: 72·85% C, 7·74% H; found: 72·63% C, 7·51% H.

3β-Benzoyloxy-5-hydroxy-19-oxo-5β,14α-card-20(22)-enolide (*XXII*)

The alcohol *XXI* (90 mg) in acetone (5 ml) was treated with Jones' reagent at 0°C for 5 min. The excess of reagent was decomposed with oxalic acid, the mixture was diluted with ether and and water, the ethereal layer was washed with water, 5% aqueous potassium hydrogen carbonate, water, dried and the solvent evaporated. The residue was crystallized from a mixture of acetone and n-heptane to yield *XXII* (46 mg), m.p. 203—204°C, $[\alpha]_D^{20}$ +25° (*c* 1·5). ^{1}H-NMR spectrum: 0·60 (3 H, s, 18-H), 4·73 (2 H, brd s, 21-H), 5·48 (1 H, m, W = 16 Hz, 3α-H), 5·83 (1 H, m, W = = 8 Hz, 22-H), 10·01 (1 H, s, 19-H). IR spectrum (KBr): 1285, 1698, 1738, 1772, 2728, 3540 cm^{-1}. For $C_{30}H_{36}O_6$ (492·6) calculated: 73·15% C, 7·37% H; found: 73·28% C, 7·24% H.

The analyses were carried out in the Analytical Laboratory of this Institute (under the direction of Dr J. Horáček). The IR *spectra were recorded by Mrs K. Matoušková and Mr P. Formánek and interpreted by Dr S. Vašíčková.* ^{1}H-NMR *spectra were recorded by Mrs J. Jelínková and Mrs M. M. Snopková. The mass spectra were recorded and interpreted by Dr F. Tureček, J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague.*

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