PREPARATION AND ABSOLUTE CONFIGURATION AT $C_{(20)}$ OF 21-NOR-5α-CHOL-22-EN-24→20-OLIDE DERIVATIVES*

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Reaction of the aldehyde *I* with the lithium salt of 1-(2-tetrahydropyranyloxy)-2-propyne yielded the compounds *II* and *IV*. From the compound *II* the lactone *XII* was prepared *via* the intermediates *III* and *X*, the lactone *XVIII* was prepared from the substance *IV via* the intermediates *V* and *XVI*. The unsaturated lactones *XII* and *XVIII* were also prepared by sulfenylation and dehydrosulfenylation of the saturated lactones *XIII* and *XIX*. Based on chemical correlation and ^{1}H-NMR spectra analyses of the compounds *II* and *IV*, the lactone *XII* was assigned the 20*R*-configuration whereas the lactone *XVIII* was allotted the 20*S*-configuration.

In our preceding paper[1] we reported the preparation of 21-nor-5α-cholane derivatives containing a γ-lactone cycle of 24→20-olide type; in the present communication we describe preparation of the corresponding derivatives with a double bond in the 22-position.

For the preparation of 3β-acetoxy-5,6-unsaturated analogs of the lactones *XII* and *XVIII*, two methods have been described up to now. The first method utilizes 3β-acetoxy-21-iodopregn-5-en-20-one as starting material to give a mixture of the corresponding unsaturated lactones in 35% yield[2]. The second method sets out from 3β-acetoxy-5,6-unsaturated derivative of the compound *XXII* and is reported to yield an unsaturated lactone but without specification whether or not the product is a mixture of $C_{(20)}$-epimers[3].

In the present paper we describe stereospecific syntheses of the isomeric lactones *XII* and *XVIII*. In the first procedure we set out from the aldehyde *I* which on reaction[4] with lithium salt of 1-(2-tetrahydropyranyloxy)-2-propyne gave *II* and *IV*. Their configuration at $C_{(20)}$ was established on the basis of their ^{1}H-NMR spectra. The signal of 18-H_3 in the derivative *IV* is situated upfield with respect to the derivative *II*. Comparison with results obtained for analogous systems[1] leads to assignment of 20*S* configuration for the compound *II* and of 20*R* configuration for the compound *IV*. Removal of the protecting group from the substance *II* gave the diol *III* which by hydrogenation over palladium on charcoal furnished the saturated diol *VII*

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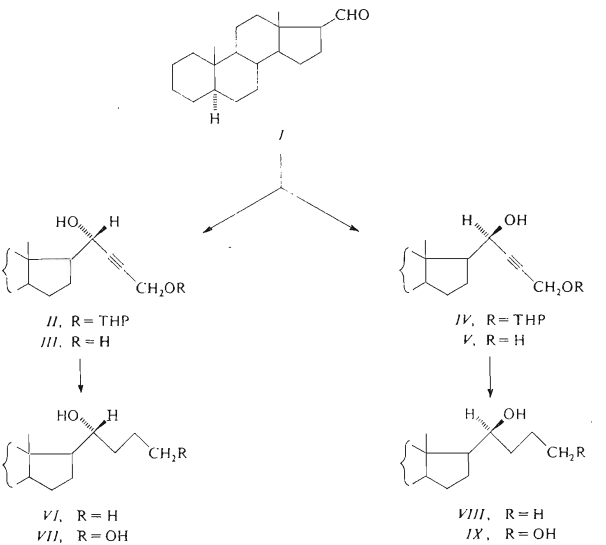
and the alcohol *VI*. Formation of the alcohol *VI* can be rationalized by hydrogenolysis of the hydroxyl group in position 24. The both hydrogenation products have been earlier found[5] to possess 20*R* configuration, this finding being in agreement with the result obtained now from an analysis of the ^{1}H-NMR spectrum. Analogously, the compound *IV* gave the diol *V* the hydrogenation of which yielded two products of 20*S* configuration, *i.e.* the diol *IX* and the alcohol *VIII*.



Partial hydrogenation of the diol *III* on P−2 nickel[6] in the presence of 1,2-diaminoethane[7] led to the unsaturated diol *X* which could be acetylated to the diacetate *XI*. The *cis* configuration of substituents on the double bond is corroborated by the respective bands in the IR-spectrum (770 cm^{-1}). The same procedure was applied to the diol *V* to give the unsaturated diol *XVI*. The latter was converted into the diacetate *XVII* the IR-spectrum of which displays a band characteristic of the *cis* arrangement of the substituents on the double bond (637 cm^{-1}). Oxidation of the diol *X* with silver carbonate on celite[8] furnished the unsaturated lactone *XII*. Its structure is confirmed by the bands at 1788, 1760 cm^{-1} in the IR-spectrum and by the signals of the 20, 22 and 23 protons in the ^{1}H-NMR spectrum (Table I).

The values of the chemical shifts, the shape of the signals and the values of the coupling constants agree with the values found for this system earlier[3]. Hydrogenation of the unsaturated lactone *XII* gave rise to the known[1] saturated lactone *XIII*. In an analogous procedure, the diol *XVI* was oxidized to the lactone *XVIII* and its hydrogenation gave the known[1] saturated lactone *XIX*. The structure of the lactone *XVIII* is corroborated by the presence of the bands in the IR-spectrum at 1793, 1785, 1763 cm^{-1}. Its ^{1}H-NMR spectrum is virtually identical with that of the epimeric lactone *XII* (Table I). In the second procedure for preparing the epimeric lactones *XII* and *XVIII* we applied a sulfenylation and dehydrosulfenylation method[9] to saturated lactones *XIII* and *XIX*. The lactone *XIII* was treated with lithium diisopropylamide to give the corresponding anion which on reaction with dimethyl disulfide gave α-methylthiolactone *XIV*. As indicated by thin layer chromatography, the reaction yields two products differing in their configurations at $C_{(23)}$. Their oxidation with *m*-chloroperoxybenzoic acid at −78°C furnished the α-methylsulfinyl lactone *XV* which on heating with calcium carbonate in toluene was converted into the unsaturated lactone *XII* in 50% overall yield with respect to the starting lactone *XIII*. Analogously, the saturated lactone *XIX* was converted *via* intermediates *XX* and *XXI* into the unsaturated lactone *XVIII* in 46% overall yield. The applied reaction sequence leads to 20*R* configuration for the lactone *XII* and to 20*S* configura-

TABLE I

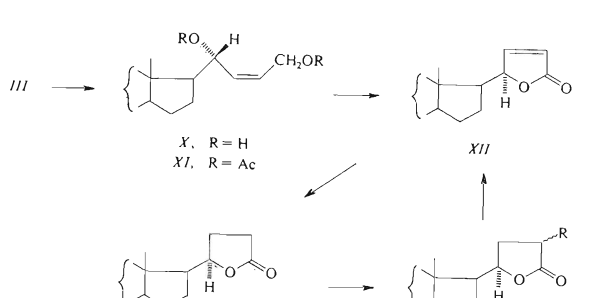
Characteristic Parameters of ^{1}H-NMR Spectra

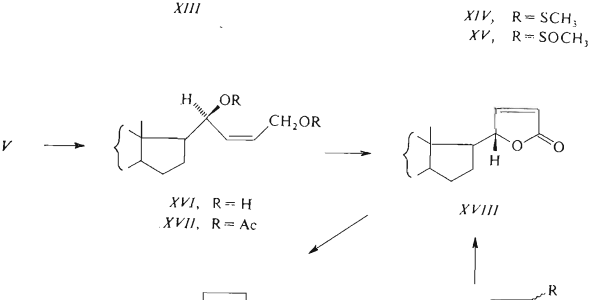
The spectra were measured in deuteriochloroform with tetramethylsilane as internal reference on Tesla B 476 (60 MHz) instrument. Chemical shifts are given in ppm (δ-scale); coupling constants (*J*) and widths of multiplets (*W*) are given in Hz. All values were obtained by first order analysis. Values in parentheses are assigned tentatively and may be mutually interchanged.

Compound	18-H_3	19-H_3	20-H	22-H	23-H	24-H_2
II[a]	0·72 s	0·78 s	4·28 mt[b]	—	—	4·28 mt[b]
IV[c]	0·67 s	0·76 s	4·28 mt	—	—	4·16 mt
XI[d]	0·67 s	0·77 s	5·43 mt[b]	5·43 mt[b]	5·43 mt[b]	4·79 mt
XVII[e]	0·63 s	0·75 s	5·47 mt[b]	5·47 mt[b]	5·47 mt[b]	4·82 mt
XII	(0·78 s)	(0·80 s)	4·93 bd[f]	7·43 dd[g]	6·06 dd [h]	—
XVIII	0·78 s[b]	0·78 s[b]	4·88 mt[i]	7·50 dd[j]	6·07 dd[k]	—

[a] Other signals 3·63 mt and 4·79 bs (tetrahydropyranyl). [b] Overlapped signals. [c] Other signals 3·62 mt and 4·81 bs (tetrahydropyranyl). [d] Other signals 1·98 s and 2·05 s (2 × CH_3COO). [e] Other signals 1·97 s and 2·03 s (2 × CH_3COO). [f] $J \simeq 5$ Hz. [g] $J_{20,22} = 1·6$ Hz, $J_{22,23} = 5·8$ Hz. [h] $J_{20,23} = 2$ Hz, $J_{22,23} = 5·8$ Hz. [i] $W \simeq 12$ Hz. [j] $J_{20,22} = 1·5$ Hz, $J_{22,23} = 5·8$ Hz. [k] $J_{20,23} = 1·9$ Hz, $J_{22,23} = 5·8$ Hz.

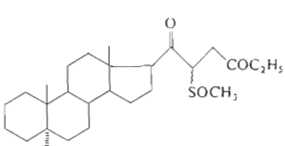
tion for the lactone *XVIII* which assignment is in line with the results of hydrogenation of the compounds *III* and *V* and with the analysis of the ^{1}H-NMR spectra of the compounds *II* and *IV*.





At last, we attempted to determine the relative proportion of the epimeric unsaturated lactones *XII* and *XVIII* in the product after reduction of the compound *XXII* with sodium borohydride. In contrast to the reaction of 3β-acetoxy-5,6-unsaturated analog of the compound *XXII*, reported in the literature[3] to give 95% yield of a product with spectroscopic properties of the unsaturated γ-lactone, reduction of the compound *XXII* gives a mixture of the lactones *XII* and *XVIII* in 47%

yield only. The attempts to separate the lactones *XII* and *XVIII* by available chromatographic methods were unsuccessful. Comparison of the $[\alpha]_D$ value (+60°) with the values found for individual lactones *XII* (+74°) and *XVIII* (−50·5°) leads to 89% and 11% content of the lactones *XII* and *XVIII*, respectively. Practically the same result 90% and 10% is obtained by comparing the respective CD curves.



XXII → *XII* + *XVIII*

EXPERIMENTAL

Melting points were determined on a Kofler block. Unless stated otherwise, optical rotations were measured in chloroform with an error of ± 3° and the IR spectra were recorded on a Zeiss UR-20 spectrometer in tetrachloromethane. The CD spectra were recorded on a Roussel–Jouan Dichrographe *II* in dioxane. Silica gel prepared according to Pitra and neutral aluminum oxide (Reanal, activity II) were used for column chromatography whereas silica gel G (Merck) was used for thin layer chromatography (TLC). Plates with 200 × 200 × 0·7 mm silica gel layer were used for preparative TLC. Usual work-up of an ethereal solution means washing the solution with dilute hydrochloric acid (1 : 4), water, saturated aqueous potassium hydrogen carbonate solution, water, drying with anhydrous sodium sulfate and evaporation of the solvent *in vacuo*. Analytical samples were dried at 50°C and 26 Pa for 12 h. The identity of the samples prepared on different routes was checked by comparison of their IR-spectra, by TLC and mixture melting point determination.

1-(2-Tetrahydropyranyloxy)-2-propyne

A solution of propargyl alcohol (43·6 ml) in dichloromethane (75 ml) was added to a mixture of dihydropyran (82·2 ml) with dichloromethane (75 ml) over a period of 30 min. At the same time, *p*-toluenesulfonic acid (110 mg) was added in three portions while the temperature was kept at +15°C. After 4 h stirring at +15°C the mixture was treated with 10% aqueous solution of potassium hydroxide (40 ml), the organic layer was separated and dried with anhydrous potassium carbonate. Distillation over a Vigreux column of 10 cm length furnished a product (70 g), b.p. 76—78°C/1·86 kPa. Literature[10] reports b.p. 71—74°C/1·60 kPa. ^{1}H-NMR spectrum (60 MHz): 1·3—2·0 broad mt (6 H); 2·48 t $J_{1,3}$ = 2·5 Hz (HC≡C); 3·25—4·10 mt (O—CH_2—); 4·22 d $J_{1,3}$ = 2·5 Hz (C≡C—CH_2O—); 4·71 bs (—OCH—O). For $C_8H_{12}O_2$ (140·2) calculated: 68·55% C, 8·63% H; found: 68·25% C, 8·59% H.

(20*S*)-24-(2-Tetrahydropyranyloxy)-21-nor-5α-chol-22-yn-20-ol (*II*)

A 1·6M solution of n-butyl lithium in n-hexane (22 ml) was added to a solution of 1-(2-tetrahydropyranyloxy)-2-propyne (5·8 g) in tetrahydrofuran (40 ml) at —78°C. The mixture was then stirred

at —20°C for 1 h, chilled to —78°C and a solution of the aldehyde[1] *I* (5 g) in tetrahydrofuran (40 ml) was added in the course of 10 min, the mixture allowed to achieve the room temperature in the course of 1 h and kept at this temperature for 2 h. The reaction was carried out while stirring under argon. After decomposition with a saturated aqueous solution of ammonium sulfate, the product was extracted with ether, the extract washed with saturated aqueous solution of ammonium sulfate, dried and evaporated. The residue was chromatographed on a column of silica gel (500 g) pre-prepared by keeping under the atmosphere of ammonia for 24 h. Light petroleum–ether (8 : 2) eluted amorphous product *II* (3·1 g), $[\alpha]_D$ —15° (*c* 2·2). IR spectrum: 3618, 3455 (OH), 1121, 1030 (C—O—C) cm^{-1}. For $C_{28}H_{44}O_3$ (428·7) calculated: 78·46% C, 10·35% H; found: 78·16% C, 10·55% H.

(20*S*)-21-Nor-5α-chol-22-yn-20,24-diol (*III*)

Water (2 ml) and *p*-toluenesulfonic acid monohydrate (120 mg) were added to a solution of the compound *II* (1 g) in methanol (40 ml). After 9 h stirring at room temperature, the solvent was removed under reduced pressure, the residue dissolved in ether and the extract washed with aqueous potassium hydrogen carbonate and with water, dried and the solvent evaporated. Crystallization of the residue from ether gave diol *III* (800 mg), m.p. 156—158°C, $[\alpha]_D$ —10·5° (*c* 2·2). IR spectrum: 3620 (OH) cm^{-1}. For $C_{23}H_{36}O_2$ (344·6) calculated: 80·18% C, 10·53% H; found: 80·36% C, 10·80% H.

(20*R*)-24-(2-Tetrahydropyranyloxy)-21-nor-5α-chol-22-yn-20-ol (*IV*)

Continued elution with light petroleum–ether (8 : 2) (preparation of the compound *II*) yielded the amorphous product *IV* (1·3 g), $[\alpha]$ +4° (*c* 3·3). IR spectrum: 3618, 3455 (OH), 1121, 1028 (C—O—C) cm^{-1}. For $C_{28}H_{44}O_3$ (428·7) calculated: 78·46% C, 10·35% H; found: 78·21% C, 10·24% H.

(20*R*)-21-Nor-5α-chol-22-yn-20,24-diol (*V*)

Preparation of the diol *V* from the compound *IV* was carried out in the same manner as preparation of the diol *III* from substance *II*. Crystallization of the residue from ether gave the diol *V* (720 mg), m.p. 170—172°C, $[\alpha]$ +15° (*c* 1·7; chloroform–methanol 1 : 1). IR spectrum: 3622 (OH) cm^{-1}. For $C_{23}H_{36}O_2$ (344·6) calculated: 80·18% C, 10·53% H; found: 80·51% C, 10·46% H.

Hydrogenation of the Diol *III*

A solution of the diol *III* (190 mg) in methanol (23 ml) and 10% palladium on charcoal (90 mg) were shaken under the atmosphere of hydrogen for 30 min. The catalyst was filtered off and the solution evaporated under reduced pressure. The residue was chromatographed on a silica gel (20 g) column. A mixture of light petroleum–ether (95 : 5) eluted the alcohol *VI* (100 mg), m.p. 146—148°C (ether) which proved identical with an autentic sample[5]. Continued elution with light petroleum–ether (1 : 1) gave the diol *VII* (40 mg), m.p. 168—170°C (ether) identical with an authentic specimen[5].

Hydrogenation of the Diol *V*

A solution of the diol *V* (100 mg) in methanol (20 ml) and 10% palladium on charcoal (80 mg) were shaken under the atmosphere of hydrogen for 30 min. The catalyst was removed by filtra-

tion and the solvent evaporated under reduced pressure. The residue was chromatographed on a silica gel (12 g) column. A mixture of light petroleum–ether (95 : 5) eluted the alcohol *VIII* (40 mg), m.p. 100—102°C (acetone), identical with an authentic sample[5]. Continued elution with light petroleum–ether (6 : 4) furnished the diol *IX* (20 mg), m.p. 183—185°C (tetrachloromethane), identical with an authentic sample[5].

(20*R*,22*Z*)-21-Nor-5α-chol-22-en-20,24-diol (*X*)

0·5 ml 1M sodium borohydride solution was prepared according to the literature[6] and added to a solution of nickel(II) acetate tetrahydrate (125 mg) in ethanol (15 ml). After 30 sec shaking under hydrogen, solutions of 1,2-diaminoethane (0·066 ml) in ethanol (1 ml) and of the diol *III* (560 mg) in ethanol (60 ml) were added. The mixture was shaken until 39 ml of hydrogen (100% of theory) were absorbed. The mixture was then passed through a silica gel (20 g) column followed by elution of the adsorbent with ethanol. Removal of the solvent and crystallization of the residue from acetone yielded the diol *X* (290 mg), m.p. 194—197°C, $[\alpha]_D$ —19° (*c* 1·4). IR spectrum (tetrachloromethane): 3624, 3490 (OH); (KBr pellet): 3020, 766 (—CH=CH—) cm^{-1}. For $C_{23}H_{38}O_2$ (346·6) calculated: 79·71% C, 11·05% H; found: 79·47% C, 11·11% H.

(20*R*,22*Z*)-21-Nor-5α-chol-22-en-20,24-diol 20,24-Diacetate (*XI*)

Acetic anhydride (2 ml) was added to a solution of the diol *X* (500 mg) in pyridine (10 ml). After 12 h standing at room temperature, the mixture was poured onto ice, the product taken up in ether and the extract worked up as usual. The crude product was chromatographed on six silica gel plates using the system light petroleum–ether (9 : 1). The obtained diacetate *XI* amounted to 450 mg, m.p. 55—58°C (light petroleum), $[\alpha]_D$ +38° (*c* 2·5). IR spectrum (carbon disulfide): 1743, 1242, 1230, 1022 (CH_3COO), 3025, 770 (—CH=CH—) cm^{-1}. For $C_{27}H_{42}O_4$ (430·6) calculated: 75·31% C, 9·83% H; found: 75·60% C, 9·78% H.

(20*R*)-21-Nor-5α-chol-22-en-24→20-olide (*XII*)

a) Silver carbonate on celite (5 g, ref.[8]) was suspended in benzene (80 ml), 10 ml of benzene was distilled off while stirring and a solution of the diol *X* (180 mg) in benzene (80 ml) was added. The suspension was stirred and refluxed for 1 h, filtered through kieselguhr and the solvent removed. The residue was chromatographed on two silica gel plates in light petroleum–ether (1 : 1) system to yield the lactone *XII* (80 mg), m.p. 185—188°C (light petroleum), $[\alpha]_D$ +73° (*c* 1·2). IR spectrum: 1788, 1760 (unsaturated lactone) cm^{-1}. CD spectrum: λ_{max} 210 nm ($\Delta\varepsilon$ +18·6). For $C_{23}H_{34}O_2$ (342·5) calculated: 80·65% C, 10·01% H; found: 80·83% C, 9·91% H.

b) A 1·6M solution of n-butyllithium in n-hexane (0·8 ml) was added to a solution of diisopropylamine (126 mg) in tetrahydrofuran (2 ml) chilled to —78°C. After 15 min cooling to —78°C there was added a solution of the lactone[1] *XIII* (120 mg) in tetrahydrofuran (3 ml). The mixture was allowed to warm to room temperature in the course of 30 min and dimethyl disulfide (105 mg) was added. The reaction was conducted with stirring under argon. After 1 h the mixture was poured into diluted hydrochloric acid, the product extracted with ether and the extract worked up as usual. As shown by TLC, the residue was a mixture of two isomers of the compound *XIV* only and was dissolved in dichloromethane (10 ml), chilled to —78°C and treated with a solution of *m*-chloroperoxybenzoic acid (71 mg of a product of 85% purity) in dichloromethane (1 ml). After 10 min stirring at —78°C, the mixture was poured into 10% aqueous sodium sulfite, the product taken up in ether and the extract washed with a sodium hydrogen carbonate solution and water. Removal of the solvent gave a residue shown by TLC to be pure compound *XV*.

The latter was dissolved in toluene (25 ml) and treated under argon with calcium carbonate (500 mg) at reflux temperature for 4 h. Salts were filtered off through a layer of kieselguhr which was then washed with ether. Evaporation of the solvent and chromatography of the residue on two silica gel plates using light petroleum–ether. (1 : 1) system yielded the lactone *XII* 60 mg, m.p. 185—187°C (light petroleum), $[\alpha]$ +75° (*c* 1·2).

(20*R*)-21-Nor-5α-cholan-24→20-olide (*XIII*)

The lactone *XII* (50 mg) in ethyl acetate (10 ml) was hydrogenated over 10% palladium on charcoal (100 mg) for two hours. The mixture was then filtered and the solvent removed *in vacuo*. Crystallization of the residue from light petroleum gave the lactone *XIII* (30 mg), m.p. 204 to 206°C, $[\alpha]_D$ —12° (*c* 2·0), identical with the authentic sample[1].

(20*S*,22*Z*)-21-Nor-5α-chol-22-en-20,24-diol (*XVI*)

Preparation of the diol *XVI* from the diol *V* was performed in the same manner as the synthesis of the diol *X* from *III*. Crystallization of the crude product from a mixture of benzene–acetone yielded the diol *XVI* (520 mg), m.p. 189—191°C, $[\alpha]_D$ —52·5° (*c* 1·9; chloroform–methanol 2 : 1). IR spectrum: 3620, 3475 (OH) cm^{-1}. For $C_{23}H_{38}O_2$ (346·6) calculated: 79·71% C, 11·05% H; found: 79·92% C, 11·39% H.

(20*S*,22*Z*)-21-Nor-5α-chol-22-en-20,24-diol 20,24-Diacetate (*XVII*)

Preparation of the diacetate *XVII* from the diol *XVI* was conducted in the same way as preparation of the diacetate *XI* from the diol *X*. The crude product was chromatographed on a silica gel column (60 g). A mixture of light petroleum–ether (92 : 8) eluted the diacetate *XVII* (483 mg), m.p. 82—85°C (light petroleum), $[\alpha]_D$ +23° (*c* 2·7). IR spectrum (carbon disulfide): 1743, 1235 (CH_3COO), 3025, 637 (—CH=CH—) cm^{-1}. For $C_{27}H_{42}O_4$ (430·6) calculated: 75·31% C, 9·83% H; found: 75·18% C, 10·05% H.

(20*S*)-21-Nor-5α-chol-22-en-24→20-olide (*XVIII*)

a) Oxidation of the diol *XVI* to the lactone *XVIII* was done in the same manner as oxidation of the diol *X* to the lactone *XII*. Chromatography of the crude product on two preparative silica gel plates using a light petroleum–ether (1 : 1) system furnished the lactone *XVIII* (90 mg), m.p. 186—188°C (light petroleum), $[\alpha]_D$ —52° (*c* 2·1). IR spectrum: 1793, 1785, 1763, 1158 (unsaturated lactone) cm^{-1}. CD spectrum: λ_{max} 210 nm ($\Delta\varepsilon$ —8·8). For $C_{23}H_{34}O_2$ (342·5) calculated: 80·65% C, 10·01% H; found: 80·45% C, 10·10% H.

b) Preparation of the lactone *XVIII* from the lactone[1] *XIX* was conducted through the intermediates *XX* and *XXI* in the same manner as preparation of the lactone *XII* from *XIII* through intermediates *XIV* and *XV*. Chromatography of the crude product on two silica gel plates in light petroleum–ether (1 : 1) gave the lactone *XVIII* (55 mg), m.p. 185—188°C (ether), $[\alpha]_D$ —49° (*c* 1·3).

(20*S*)-21-Nor-5α-cholan-24→20-olide (*XIX*)

Hydrogenation of the lactone *XVIII* to *XIX* was conducted in the same manner as hydrogenation of the lactone *XII* to *XIII*. Crystallization of the crude product from light petroleum yielded the lactone *XIX* (32 mg), m.p. 193—195°C, $[\alpha]_D$ +25° (*c* 2·0), identical with the authentic sample[1].

Reduction of the Compound *XXII* with Sodium Borohydride

A solution of the crude *XXII* (500 mg, ref.[5]) in methanol (4 ml) and dichloromethane (2·5 ml) was cooled to 0°C. After addition of sodium borohydride (100 mg) the mixture was stirred and kept at 0°C for 2 h, diluted with ethyl acetate (200 ml) and washed with 2M aqueous solution of sodium hydroxide (2×), saturated aqueous ammonium chloride solution (2×) and with water. The crude product was chromatographed on silica gel column (50 g). A mixture of light petroleum–benzene–ether (49 : 49 : 2) eluted a mixture of the lactones *XII* and *XVIII* (180 mg), m.p. 179—185°C (light petroleum), $[\alpha]_D$ +60° (*c* 1·0). IR spectrum: 1788, 1760 (unsaturated lactone) cm^{-1}. CD spectrum: λ_{max} 210 nm ($\Delta\varepsilon$ +15·9). For $C_{23}H_{34}O_2$ (342·5) calculated: 80·65% C, 10·01% H; found: 80·53% C, 10·12% H.

The analyses were carried out in the Analytical Laboratory of this Institute (head Dr J. Horáček). The infrared spectra were recorded by Mrs K. Matoušková and Mr P. Formánek and interpreted by Dr S. Vašíčková. The CD *spectra were recorded and interpreted by Dr S. Vašíčková. The* ^{1}H-NMR *spectra were recorded by Mrs J. Jelínková.*

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