ON STEROIDS. CIL.*

A-HOMOSTEROIDS. III. PREPARATION AND REACTIONS OF 4α,4aα-EPOXY-A-HOMO-5α-CHOLESTAN-6β-YL ACETATE

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Preparation of 4α,4aα-epoxy-A-homo-5α-cholestan-6β-yl acetate is described; participation of the 6β-acetoxy group in reactions involving 4α,4aα-epoxide ring fission is reported.

In the preceding papers[1,2], we have reported preparation and structure proof of some A-ring substituted derivatives of 6β-acetoxy-A-homo-5α-cholestan-4-one. In the present paper we describe further transformations of the A-ring, the first aim being the preparation of 4,4a-unsaturated compound suitable as starting material for the introduction of various substituents into the positions 4 and 4a.

However, the attempt at preparing the desired olefine *IV* by treating the bromohydrine[1] *I* with zinc in ethanol failed; instead, the reaction afforded the known[1] ketone *III*. This result is surprising since preparation of olefins from bromohydrins by treatment with zink in ethanol is known to be a nonstereospecific reaction[3-5] affording olefins both from *cis* and *trans* bromohydrins. At first glance, formation of the ketone *III* seems to be related to the fact that several conformations of the A-ring are possible in which the $C_{4(a\alpha)}$-bromine atom and hydrogen at $C_{(4\beta)}$ occupy *anti*-periplanar orientation thus providing optimal conditions for the formation of the ketone *III*. However, this cannot provide a satisfactory explanation for exclusive formation of the ketone *III* since many other cases are known[3] in which an olefin is formed although *anti*-periplanar arrangement of bromine and hydrogen atoms is also present in the respective compounds. Similar formation of ketones rather than of the expected alcohols was observed by Clarke and Daum[6] on catalytic dehalogenation of some bromohydrins. For explanation of this behavior a free radical mechanism was postulated requiring parallel position of the single electron orbital with the hydrogen attached at the carbon atom bearing the hydroxyl group. As can be demonstrated on models, the necessary conformational arrangement is possible in our case. Indeed, we observed[2] formation of the ketone *III* (along with the expected alcohol in 1 : 1 poportion) from the bromohydrine *I* on catalytic dehalogenation. Assumption of similar free radical mechanism on zinc–ethanol treatment of *I* would need additional support; it thus remains a possible, but certainly not an ensured, pathway.

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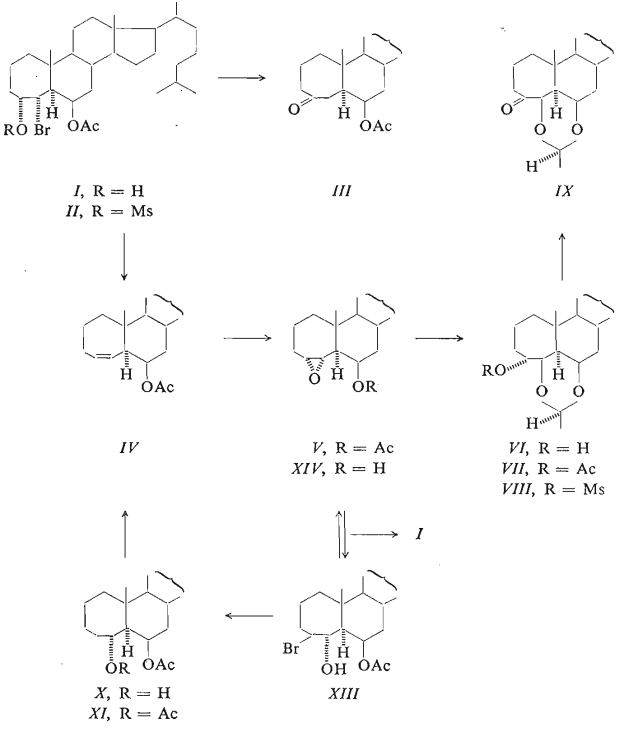
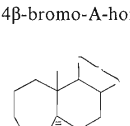
The desired olefin *IV* was then prepared in the alternative manner: the bromohydrin *I* was transformed into the methanesulphonyloxy derivative *II* which gave the olefin *IV* in 83% yield on treatment with sodium iodide. Alternatively, it could also be obtained by dehydrating the alcohol *X* with thionyl chloride.

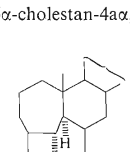
Oxidation of the unsaturated compound *IV* with perphthalic acid afforded an epoxide in 80% yield. Analogously to the steric course of epoxidation in A-ring of normal steroids, the α-configuration for the epoxide appeared most probable; this assumption was proved by the following correlation with the known A-homocholestane derivatives[1]: fission of the epoxide ring with hydrobromic acid yielded a mixture of two bromohydrins in about 1 : 1 proportion. Since the more polar bromohydrin was



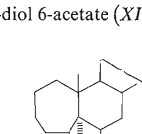
shown to be identical with the known[1] 4aα-bromo-A-homo-5α-cholestan-4α,6β-diol 6-acetate (*I*) the parent epoxide must be formulated as 4α,4aα-epoxy-A-homo-5α-cholestanyl 6β-acetate (*V*). The somewhat unusual formation of the *cis*-bromohydrin by the epoxide ring fission can be rationalized as a reaction involving participation of the 6β-acetoxy group. Participation of the neighboring acetoxy group in epoxide ring fission was observed in several instances[7-11,14]. The second bromohydrin was subjected to catalytic dehydrohalogenation to yield an alcohol which is not identical with any of the known 4-epimeric alcohols[1]; consequently, the alcohol in question must be 4aα-hydroxy derivative *X* (characterized also as the acetate *XI*). This second bromohydrin reacts with methanolic potassium hydroxide to give the epoxide *XIV* obtainable also by hydrolysis from the acetate *V*. These reactions prove the formula of 4β-bromo-A-homo-5α-cholestan-4aα,6β-diol 6-acetate (*XIII*).



XV



XVI



XVII

The main product of the hydrogenolytic fission of the epoxide *V* is – along with the expected 4aα-hydroxy derivative *X* – the substance *VI* which was characterized as the acetate *VII* and the methanesulphonyloxy derivative *VIII*. Structure of the compound *VI* was proved by combination of physical and chemical methods: the IR-spectrum of the acetyl derivative *VII* exerted a strong acetal band at 1125 cm^{-1}. The mass spectrum demonstrated the molecular weight of 502; the fragment of *m/e* 398 arises from the ion of *m/e* 442 by splitting off one molecule of acetaldehyde (m* 358·2 : $442^+ \rightarrow 398^+ + 44$) which result is in agreement with the presence of an acetal grouping in the molecule. Similarly, the NMR-spectrum is in line with the structure of the compound *VII* as an acetoxy acetal. This follows from the presence of a secondary methyl group ($\delta = 1{\cdot}29$ p.p.m., $J = 4{\cdot}9$ Hz) and from the position and splitting pattern of the signal characteristic of the $\begin{matrix} O \\ O \end{matrix}\!\!>\!CH.CH_3$ moiety ($\delta =$ 4·72 p.p.m., $J = 4{\cdot}9$ Hz).

Absence of coupling between the $>\underline{CH}—O—CH(CH_3)—O—\underline{CH}<$ protons and the presence of coupling between one of these protons and —CH—OAc proton excludes any formula with adjacent carbon atoms bearing the acetal oxygens, *e.g. XV*. However, the alternate formula *XVI*, could not be excluded in this manner but confirmation of the structure *VII* (and *VI* for the free alcohol) was provided by the analysis of the NMR-data of the keto derivative *IX* obtained from

VI. The signal of one of the —OCH< protons of this ketone is present as a doublet (δ = 4·18 p.p.m., J = 3·5 Hz) which is only possible for the structure *IX*. Formation of the acetal *VI* by hydrogenolysis of the epoxide *V* in the presence of acetic acid can be explained by participation of the 6β-acetoxy group involving intermediate formation of the acetoxonium ion *XVII*. Participation of the acetoxy group in epoxide ring fission and reduction of the intermediate acetoxonium ion salt to the corresponding acetal upon the action of complex hydrides was observed by other authors[12,13].

The last question is the geometry of the six-membered acetal ring. We assume the chair conformation for this ring. In this conformation (Fig. 1), the upper tip of the chair is represented by the $C_{(5)}$-carbon atom whereas the opposite tip, represented by the acetal carbon atom, is directed downwards. Thus, the steric interaction of any substituent at this carbon with the $C_{(19)}$-angular methyl group is out of question; even a β-oriented grouping, being equatorial, is far from the $C_{(19)}$-methyl. From the two possible configurations of the secondary methyl group, the β-orientation is favored for complete absence of any crowding, whereas the alternative α-configuration is less probable owing to two 1,3-diaxial interactions of the methyl group with 4aα- and 6α-hydrogen atoms. Therefore, we formulate the respective compounds with β-oriented methyl group as represented by the formulae *VI*—*IX*.

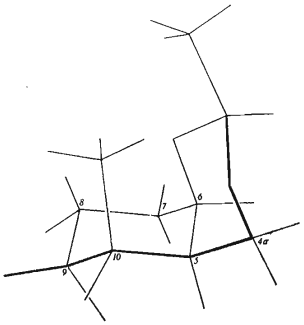


FIG. 1
Conformation of the Acetal Ring

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Unless stated otherwise, optical rotations were measured in chloroform. The infrared spectra were measured on a Zeiss UR 10 spectrophotometer. The NMR spectra were measured in deuterated chloroform on Varian HA-100 apparatus using tetramethylsilane as internal reference. Chemical shifts are expressed in δ-scale. The multiplicity of the signals is reported using the following symbols: s singlet, d doublet, dd doublet of doublets, t triplet, m multiplet, b broad, W width of a multiplet, W 1/2 half-width of a signal. The identity of samples prepared by different routes was checked by a mixture-melting points determination and by infrared spectra. The statement "worked up as usual" stands for: The solution was washed with water, 5% hydrochloric acid, water, 5% $KHCO_3$, water, dried with sodiun sulfate and the solvent evaporated *in vacuo*.

Reaction of 4aα-Bromo-A-homo-5α-cholestan-4α,6β-diol 6-yl Acetate (*I*)

The bromohydrin *I* (150 mg) in ethanol (15 ml) was refluxed with zinc dust (750 mg) activated with hydrochloric acid for 8 h. Zinc was filtered off, washed with ether and the combined filtrates evaporated *in vacuo*. The residue was dissolved in ether and worked up as usual. The residue (140 mg) was chromatographed preparatively on three plates of silica gel (20 × 20 cm) in light petroleum–acetone (9 : 1). The corresponding zones were collected, eluted with ether and the solvent was evaporated *in vacuo*. The residue (80 mg) afforded after crystallization from methanol 50 mg of 6β-acetoxy-A-homo-5α-cholestan-4-one(*III*), m.p. 125—127°C, $[\alpha]_D^{22}$ +49° (*c* 1·0) in accordance with literature[1].

4α-*Methanesulphonate* II: The monoacetate *I* (200 mg) in pyridine (5·0 ml) was treated with with methanesulphonyl chloride (1·3 ml) at 0°C for 18 h. The reaction mixture was then decomposed with ice, the product taken up in ether. The ethereal was worked up as usual to give the oily residue (200 mg). IR-spectrum (tetrachloromethane): 1742, 1370, 1240, 1180 cm^{-1}.

6β-Acetoxy-A-homo-5α-cholest-4-ene (*IV*)

a) The oily methanesulphonate *II* (2·5 g) in methyl ethyl ketone (50 ml) was treated with sodium iodide (7·5 g), the mixture was refluxed for 8 h and then allowed to stand overnight. The mixture was poured into water, the product was taken up in ether. The ethereal extract was washed with water, dried over sodium sulfate and evaporated *in vacuo*. The residue (2·5 g) was chromatographed on silica gel (50 g) in light petroleum–acetone (99 : 1) to give the oily olefin *IV* (1·5 g). IR spectrum (tetrachloromethane): 3020, 1736, 1655, 1245, 1029 cm^{-1}. NMR: 0·70 (s, 3 H, 18-CH_3); 0·94 (s, 3 H, 19-CH_3); 0·87 (d, J = 6 Hz, 6 H, 26, 27-CH_3); 0·91 (d, J = 6 Hz, 3 H, 21-CH_3); 2·06 (s, 3 H, OAc); 5·80 (mt, 1 olefinic H); 5·23 (dd, splittings 4 and 10 Hz), 1 olefinic H); 5·02 (mt, W = 10 Hz, 1 H, CH—OA); 2·47 (mt, 5α-H). For $C_{30}H_{50}O_2$ (442·7) calculated: 81·39% C, 11·38% H; found: 81·59% C, 11·24% H. *b*) A solution of the alcohol *X* (50 mg) in pyridine (1·5 ml) was cooled to 0°C and treated with the solution of 0·15 ml thionyl chloride (freshly distilled) in 0·7 ml pyridine. The reaction mixture was allowed to stand at 0°C for 1 h, then poured into water and the product extracted with ether. The ethereal extract was worked up as usual. The residue (45 mg) was preparatively chromatographed on one plate of silica gel (20 × 20 cm) in light petroleum–acetone (98 : 2). The corresponding zone was collected, extracted with ether and the solvent evaporated *in vacuo*. The oily residue (19 mg) resisted all attemps at crystallization. The identity with the above sample was proved by IR- and NMR-spectra.

4α,4aα-Epoxy-A-homo-5α-cholestan-6β-yl Acetate (*V*)

The olefin *IV* (1·2 g) in ether (20 ml) was treated with a solution of perphthalic acid (1·6 g) in ether (15 ml) and set aside at room temperature for 18 h. The reaction mixture was diluted with ether, the excess of peracid was extracted into 5% $KHCO_3$, the ethereal solution was washed with water, dried over sodium sulfate and evaporated *in vacuo*. The residue (1·25 g) afforded after recrystallization from methanol 1·0 g of the epoxide *V*, m.p. 107—109°C, $[\alpha]_D^{25}$ −25·6° (*c* 0·9). Infrared spectrum (tetrachloromethane): 1740, 1240, 1029, 856 cm^{-1}. NMR: 0·68 (s, 3 H, 18-CH_3); 1·03 (s, 3 H, 19-CH_3); 0·85 (d, J = 6 Hz, 6 H, 26, 27-CH_3); 0·89 (d, J = 6 Hz, 3 H; 21-CH_3); 2·07 (s, 3 H, OAc); 5·25 (mt, 1 H, CH—OAc), 2·87 (dd, $J_{4a,5}$ = 7·7 Hz, $J_{4a,4}$ = 4·7, 1 epoxydic H); 3·13 (mt, 1 epoxydic H). For $C_{30}H_{50}O_3$ (458·7) calculated: 78·49% C, 10·99% H; found: 78·63% C, 11·29% H.

4aβ,6β-Ethylidenedioxy-A-homo-5α-cholestane-4α-ol (*VI*)

The epoxide *V* (100 mg) in glacial acetic acid (5·5 ml) was agitated in a hydrogen atmosphere over Adams'catalyst (100 mg) for 8 hours. Catalyst was filtered off, washed with ether, and the filtrate was washed with water, 5% $KHCO_3$, water, dried over sodium sulfate and evaporated *in vacuo*. The residue (100 mg) was preparatively chromatographed on two plates of silica gel (20 × 20 cm) in light petroleum–acetone (9 : 1). The corresponding zones were collected, eluted with ether and the solvent evaporated *in vacuo*. The residue (51 mg) on repeated crystallization from heptane yielded 39·5 mg of the alcohol *VI*, m.p. 141—143°C, $[\alpha]_D^{22}$ +55·1° (*c* 0·5). IR-spectrum (tetrachloromethane): 3600, 1130, 1037 cm^{-1}. For $C_{30}H_{52}O_3$ (460·7) calculated: 78·20% C, 11·38% H; found: 76·70% C, 11·19% H.

4aβ,6β-Ethylidenedioxy-Á-homo-5α-cholestan-4α-yl Acetate (*VII*)

The alcohol *VI* (50 mg) was acetylated with acetic anhydride (0·2 ml) in pyridine (1 ml) for 20 h at room temperature. Usual working up gave 50 mg of a crude product which was preparatively chromatographed on one plate of silica gel (20 × 20 cm) in light petroleum. The corresponding zone was collected, eluted with ether and the solvent evaporated *in vacuo*. The residue (35 mg) on crystallization from methanol yielded 20 mg of the acetate *VII*, m.p. 150—151°, $[\alpha]_D^{23}$ +50·2° (*c* 0·5). Mass spectrum: 502. IR-spectrum (tetrachloromethane): 1739, 1250, 1238, 1036, 1125 cm^{-1}. NMR: 0·69 (s, 3 H, 18-CH_3); 1·06 (s, 3 H, 19-CH_3); 0·865 (d, J = 6 Hz, 6 H, 26, 27-CH_3); 0·905 (d, J = 6 Hz, 3 H, 21-CH_3); 2·03 (s, 3 H, OAc); 1·28 (d, J = 4·9 Hz, 3 H, >CH—CH_3); 3·71 (broad q, 1 H, —O>CH—CH<O—); 3·86 (q, 1 H, —O>CH—CH<O—); 4·72 (q, J = = 4·9 Hz, 1 H, O>CH—CH_3); 4·94 (broad mt, W ~30 Hz, 1 H, CH—OAc). For $C_{32}H_{54}O_4$ (502·75) calculated: 76·44% C, 10·83% H; found: 76·11% C, 10·92% H.

4α-Methanesulphonyloxy-4aβ,6β-ethylidenedioxy-A-homo-5α-cholestane (*VIII*)

The alcohol *VI* (80 mg) in pyridine (2 ml) was treated with methanesulphonyl chloride (0·05 ml) at 0°C for 2 h. The reaction mixture was then decomposed with ice, the product taken up in ether. The ethereal extract was worked up as usual. The residue (70 mg) on crystallization from heptane afforded 55 mg of the methanesulphonyloxy derivative *VIII*, m.p. 146—148°C. Infrared spectrum (tetrachloromethane): 1179, 1366, 1130, 1120, 1142, 942 cm^{-1}. For $C_{31}H_{54}O_5S$ (538·8) calculated: 69·09% C, 10·10% H; found: 68·44% C, 10·45% H.

4aβ,6β-Ethylidenedioxy-A-homo-5α-cholestan-4-one (*IX*)

A solution of the alcohol *VIII* (40 mg) in pyridine (1 ml) was dropwise added to chromium trioxide (20 mg)–pyridine (1 ml) complex and allowed to stand at room temperature for 48 h. The mixture was then diluted with ether, poured into water and the product extracted with ether. The ethereal extract was worked up as usual. The residue (35 mg) was chromatographed preparatively on one plate of silica gel (20 × 20 cm) in benzene–ether (85 : 15). The corresponding zone was collected, eluted with ether and the solvent evaporated *in vacuo*. The residue (15 mg) on crystallization from methanol afforded 9 mg of the ketone *IX*, m.p. 191—194°C. Infrared spectrum (KBr disc): 1720, 1159, 1127, 1179, 1111 cm^{-1}. NMR: 0·79 (s, 3 H, 18-CH_3); 0·885 (s, 3 H, 19-CH_3); 0·86 (d, J = 6·0 Hz, 6 H, 26,27-CH_3); 0·89 (d, J = 6·0 Hz, 3 H, 21-CH_3); 1·415 (d, J = 5 Hz, 3 H, CH_3—CH); 3·81 (mt, 1 H, OCH); 4·18 (d, J = 3·5 Hz, 1 H, OCH); 4·775 (q, J = 5·0 Hz, 1 H, (O_2CH—CH_3); 2·51 (mt, 2 H, two distinct H's). For $C_{30}H_{50}O_3$ (458·7) calculated: 78·55% C, 10·99% H; found: 78·25% C, 10·69% H.

A-Homo-5α-cholestan-4aα,6β-diol 6-Acetate (*X*)

a) After chromatographic separation of the alcohol *VI* from the hydrogenolytic reaction of the epoxide *V*, the less polar corresponding zones were collected, eluted with ether and the solvent evaporated *in vacuo*. On crystallization from methanol, the oily residue (29 mg) gave 17·8 mg of the monoacetate *X*, m.p. 122—123°C, $[\alpha]_D^{25}$ +0·5° (*c* 0·8). IR-spectrum (tetrachloromethane): 3510, 1723, 1717, 1265, 1242 cm^{-1}. NMR: 0·71 (s, 3 H, 18-CH_3); 0·90 (s, 3 H, 19-CH_3); 0·865 (d, J = 6·0 Hz, 6 H, 26, 27-CH_3); 0·905 (d, J = 6·0 Hz, 3 H, 21-CH_3); 2·09 (s, 3 H, OAc); 5·49 (unresolved mt, 1 H, CH—OAc); 3·45 (broad unresolved mt, 1 H, CH—O). For $C_{30}H_{52}O_3$ (460·7) calculated: 78·20% C, 11·38% H; found: 77·74% C, 10·98% H. *b*) The bromohydrin *XIII* (63 mg) in ethyl acetate (7 ml) and ethanol (3 ml) was agitated in a hydrogen atmosphere over 5% palladium-on-calcium-carbonate catalyst (200 mg) for 6 h. The mixture was then diluted with ether, the catalyst was filtered off, washed with ether and the filtrate evaporated *in vacuo*. The residue (55 mg) was preparatively chromatographed on one plate of silica gel (20 × 20 cm) in light petroleum–acetone (85 : 15). The corresponding zone was collected, eluted with ether and the solvent evaporated *in vacuo*. After recrystallization from methanol at 0°C the residue (24 mg) afforded 17 mg of the monoacetate *X*, m.p. 122—123°C, $[\alpha]_D^{21}$ +0·5° (*c* 1·0).

A-Homo-5α-cholestane-4aα,6β-diol Diacetate (*XI*)

The monoacetate *X* (45 mg) was acetylated with acetic anhydride (0·2) in pyridine (1 ml) for 48 h at room temperature. Usual working up gave 51 mg of oily product, which on crystallization from methanol yielded 28·5 mg of the diacetate *XI*, m.p. 107—108·5°C, $[\alpha]_D^{23}$ +3·5° (*c* 0·5). Infrared spectrum (tetrachloromethane): 1738, 1257, 1038, 1020 cm^{-1}. For $C_{32}H_{54}O_4$ (502·75) calculated: 76·44% C, 10·83% H; found: 76·23% C, 10·92% H.

4β-Bromo-A-homo-5α-cholestan-4aα,6β-diol 6-Acetate (*XIII*)

The epoxide *V* (300 mg) in chloroform (4 ml) was treated with 48% HBr (1 ml) and agitated at room temperature for 45 min. The reaction mixture was diluted with water, the product taken up into ether, and the ethereal extract was washed with 5% $KHCO_3$, water, dried over sodium sulfate and evaporated *in vacuo*. The residue (300 mg) was chromatographed on a silica gel column (45 g) in light petroleum–acetone (99 : 1) to give two separated fractions. The first one, less polar, afforded after crystallization from methanol at 0°C 120 mg of the bromohydrin *XIII*, m.p. 115—117°C, $[\alpha]_D^{23}$ +17·2° (*c* 0·5). IR-spectrum (tetrachloromethane): 3568, 1738, 1250 cm^{-1}. For $C_{30}H_{51}BrO_3$ (539·53) calculated: 66·77% C, 9·52% H; found: 67·37% C, 9·35% H. On crystallization from methanol, the second fraction (125 mg) yielded 100 mg of the bromohydrin *I*, m.p. 60—62°C, $[\alpha]_D^{21}$ −10° (*c* 1·0) in accordance with the literature[1].

4α,4aα-Epoxy-A-homo-5α-cholestan-6β-ol (*XIV*)

a) The bromohydrin *XIII* (38 mg) was added to a solution of potassium hydroxide (600 mg) in methanol (10 ml) and refluxed for 1 h. Methanol was then distilled off under reduced pressure, the residue was diluted with water, and the product extracted into ether. The ethereal extract was washed with water, dried over sodium sulfate and evaporated *in vacuo*. The residue (37·5 mg) on crystallization from methanol at 0°C yielded 20 mg of the epoxide *XIV*, m.p. 157—159°C, $[\alpha]_D^{23}$ +13·9° (*c* 0·5). Infrared spectrum (tetrachloromethane): 3625, 1042, 855 cm^{-1}. For $C_{28}H_{46}O_2$ (414·65) calculated: 81·10% C, 11·18% H; found: 80·83% C, 11·42% H. *b*) To a solution of the epoxide *V* (90 mg) in methanol (10 ml) was added solid potassium KOH hydroxide (100 mg) and the reaction mixture was refluxed for 3 h. Methanol was distilled off under reduced

pressure, the residue diluted with water and the product was extracted into ether. The ethereal extract was washed with water, dried over sodium sulfate and evaporated *in vacuo*. The residue (88 mg) on crystallization from methanol at 0°C afforded 59·5 mg of the alcohol *XIV*, m.p. 157—158·5°C, $[\alpha]_D^{21}$ +14° (*c* 1·0).

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