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147. Yasuhiro Morisawa : Steroid Series. XII.*1 Stereochemistry of B-Nor-5β,8α-steroid Derivatives.

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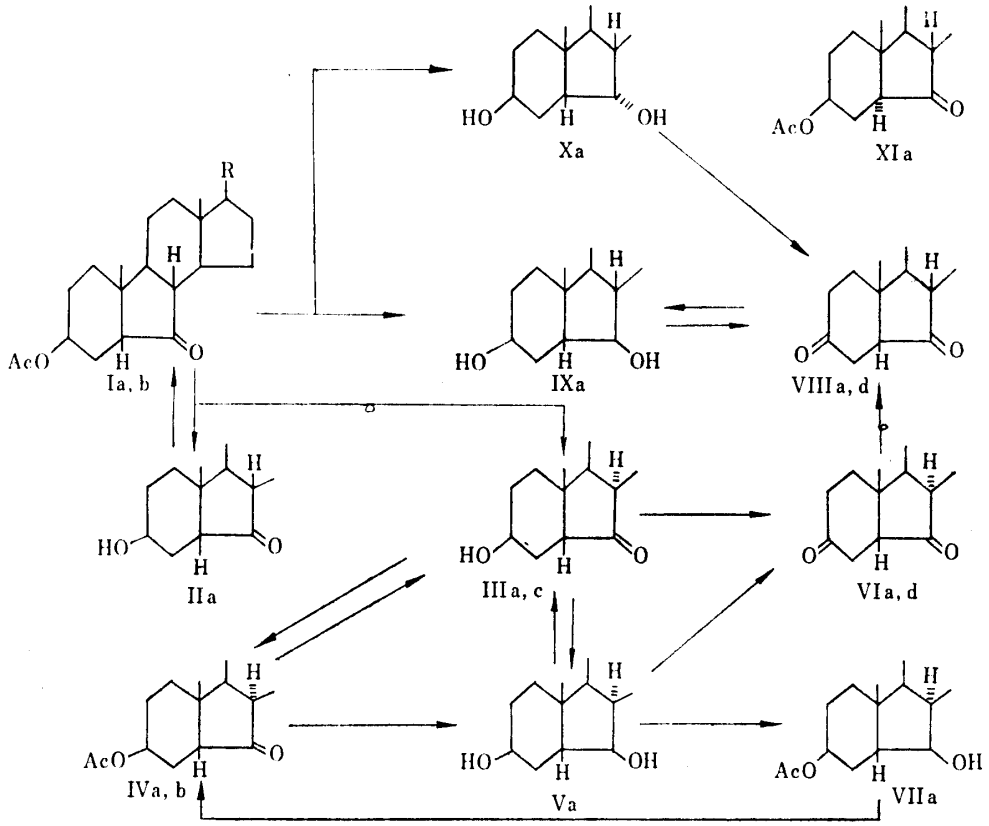
Dauben and his associates[1] observed a base-induced isomerization of B-nor-5β-cholestan-6-one and its 3-hydroxyl or 3-acetoxyl derivative (Ia) into keto-compounds possessing an unnatural C_8-α-configuration. On the other hand the 3,6-diketone (Va) with 8α-hydrogen was found to isomerize into the dione (VIIIa) with the natural 8β-configuration. This marked change in the thermodynamic stability about B/C ring juncture between the two series of compounds was attributed to the long range conformational effects induced by a change of hybridization at C_3 from trigonal to tetrahedral state.[2]

The assignment of the 8α-configuration to the isomeric ketol (III) was first deduced by examination of its rotatory dispersion curve[1] and recently confirmed by chemical means[2] but the configuration of the A/B ring juncture still remains to be studied.

In our brief report[3] on the synthesis of 7-aza-5β-cholestanol involving Beckmann rearrangement of 3β-acetoxy-B-nor-5β-cholestan-6-one (Ia), we tentatively assigned the



a : R=C_8H_{17} b : R=OAc c : R=OH d : R=O

Chart 1.

*1 Part XI : This Bulletin, **11**, 536 (1963).

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1) W. G. Dauben : Bull. soc. chim. France, **1960**, 1338.

2) W. G. Dauben, G. A. Boswell, Jr., N, Templeton, J. W. McFarland : J. Am. Chem. Soc., **85**, 2302 (1963).

3) Y. Morisawa, Y. Kishida, K. Tanabe : This Bulletin, **11**, 686 (1963).

5β,8α-configuration to Dauben's ketol (IIIa) on the basis of the conformational analysis. The present paper will describe further support for our assignment and also discuss the conformation of the A and C rings of the ketol, based on examination of the nuclear magnetic resonance spectra of the isomeric ketol and related compounds in the cholestane and androstane series.

Inspection of Dreiding model shows that the B/C-*cis*-configuration permits the ring C to take either the chair or boat forms and consequently four conformations, A_1 and A_2 for A/B-*cis*, A_3 and A_4 for A/B-*trans* configuration, can most favourably exist as shown in Chart. 2.

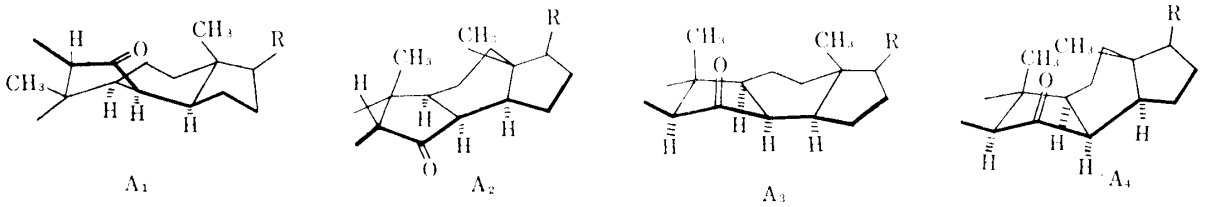

Chart 2.

The chemical shifts observed for the C_{18}-methyl protons of the isomeric 6-keto compounds all appear at a high field by 0.11~0.21 p.p.m. than those of the corresponding 8β-derivatives as listed in Table I. This can be reasonably explained in terms of the diamagnetic shift caused by C_6-carbonyl group, since in these conformations the C_{18}-methyl group lies in conical regions extending above the plane of the carbonyl group[4]. This shielding effect can not be anticipated in the ketol of 8β-configuration, where the C ring is compelled to take a chair form. These observations, therefore, add further support for Dauben's configurational assignment to the C_8-center of the isomeric ketol.

TABLE I. 18-Methyl Proton Resonance of B-Nor-androstan- and Cholestan-6-one Derivatives

Substance	18-H (τ)	Difference (8α-8β) (p.p.m.)
3β-Acetoxy-B-nor-5β,8β-cholestan-6-one (Ia)	9.35	+0.15
3β-Acetoxy-B-nor-5β,8α-cholestan-6-one (IVa)	9.50	
3β-Hydroxy-B-nor-5β,8β-cholestan-6-one (IIa)	9.36	+0.11
3β-Hydroxy-B-nor-5β,8α-cholestan-6-one (IIIa)	9.47	
B-Nor-5β,8β-cholestane-3,6-dione (VIIIa)	9.32	+0.14
B-Nor-5β,8α-cholestane-3,6-dione (VIa)	9.46	
3β,17β-Diacetoxy-B-nor-5β,8β-androstan-6-one (Ib)	9.20	+0.17
3β,17β-Diacetoxy-B-nor-5β,8α-androstan-6-one (IVb)	9.37	
B-Nor-5β,8β-androstane-3,6,17-trione (VIIId)	9.07	+0.21
B-Nor-5β,8α-androstane-3,6,17-trione (VId)	9.28	

Of the four conformations described above, conformation A_3 possessing the C-ring in a chair form is the least probable due to very strong ring strain in the molecule; conformation A_4 with a boat C-ring might be also excluded because of considerable non-bonded interaction between the methyl groups at C_{10}- and C_{13}-positions, whatever the

4) L.M. Jackman: "Applications of NMR spectroscopy in Organic Chemistry," p. 119, Pergamon Press, New York (1959).

conformation of ring-A. Conformations A_1 and A_2 with the C-ring in a chair and boat form respectively, can be assumed without strain and in the former no steric interaction between the two angular methyl groups exists, irrespective of either possible A-ring conformation. Conformation A_2 shows considerable interaction between the two methyl groups except in the case of the 3β-equatorial chair conformation of the A-ring, where, however, crowding between C_{18}-methyl group and 5β-hydrogen would subsequently arise. Therefore, conformation A_1 with A/B *cis* configuration seems to be most likely for the isomeric ketol.

The nuclear magnetic resonance data for the 3α-proton are consistent with the above A/B *cis* assignment to the 8α-ketol. As seen in Table II, the signals for the 3α-protons in 3β-hydroxy-B-nor-5β,8α-cholestan-6-one (IIIa) and its acetate (IVa) appear at 6.66 and 5.48 τ, respectively. Inspection of Dreiding model clearly shows that 3β-acetoxy-B-nor-5α,8β-cholestan-6-one (XI) possesses an A-ring chair conformation with an axial 3α-proton exhibits peak at 5.16 τ. It is well established that the chemical shift for an axial proton appears at a higher field than that for an equatorial one due to the anisotropic effect of carbon-carbon bond.[5] The higher field resonance for the 3α-proton in the 8α-H-ketol than that for the axial 3α-proton in XI suggests that the proton should be located in a field influenced by the anisotropy of C-C bond and/or the C_6-carbonyl function.

Table II. Resonance of 3α-Proton Resonance of B-Norcholestan-6-one Derivatives

Substance	3α-H
3β-Acetoxy-B-nor-5α,8β-cholestan-6-one (XI)[a]	5.16
3β-Acetoxy-B-nor-5β,8β-cholestan-6-one (Ia)	4.96
3β-Acetoxy-B-nor-5β,8α-cholestan-6-one (IVa)	5.48
3β-Hydroxy-B-nor-5β,8β-cholestan-6-one (IIa)	5.95
3β-Hydroxy-B-nor-5β,8α-cholestan-6-one (IIIa)	6.66

a) The preparation of the compound will be described in the forthcoming paper (This Bulletin).

The possible conformation for the 8α-H-ketol acetate are shown in Fig. 3. The equatorial 3α-proton in conformations B_2, B_3, or B_4 would exhibit a signal in lower field than that of 3β-acetoxy-B-nor-5α-cholestan-6-one (XI) and the axial proton resonance in conformation B_1 would be expected to appear 5.16 τ, since the axial proton lie sterically in about the same environment as those in XI.[6] While in conformation B_5 or B_6, the 3α-proton exists in axial orientation and moreover lies in the effective diamagnetic field due to the C_6-carbonyl group. The higher values observed for the 3α-proton resonance in the 8α-H-ketol and its acetate are only explainable by conformation B_5 or B_6.

The ketol acetate (Ia, b) was synthesized according to the method of Joska, *et al.*[7,8] and treated either with alkali or acid to afford an epimeric mixture of 3β-hydroxy-6-oxo-B-nor-5β,8β-steroid compound (IIa, b) and the 8α-H-isomer (IIIa, c). The separation of the epimers in the androstane series was effected by acetylation and subsequent chromatography over alumina. The ketol (IIa, b) re-acetylated back to the parent acetate (Ia, b), while the ketol (IIIa, c) gave a new acetate (IVa, b).

5) L. F. Jackman: "Applications of NMR Spectroscopy in Organic Chemistry," p. 115, Pergamon Press, Now York (1959).
6) J. N. Shoolery, Max T. Rogers: J. Am. Chem. Soc., 80, 5121 (1958).
7) J. Joska, J. Fajkoš, F. Šorm: Collection Czechoslov. Chem. Communs., 28, 82 (1963).
8) *Idem*: *Ibid.*, 28, 605 (1963).

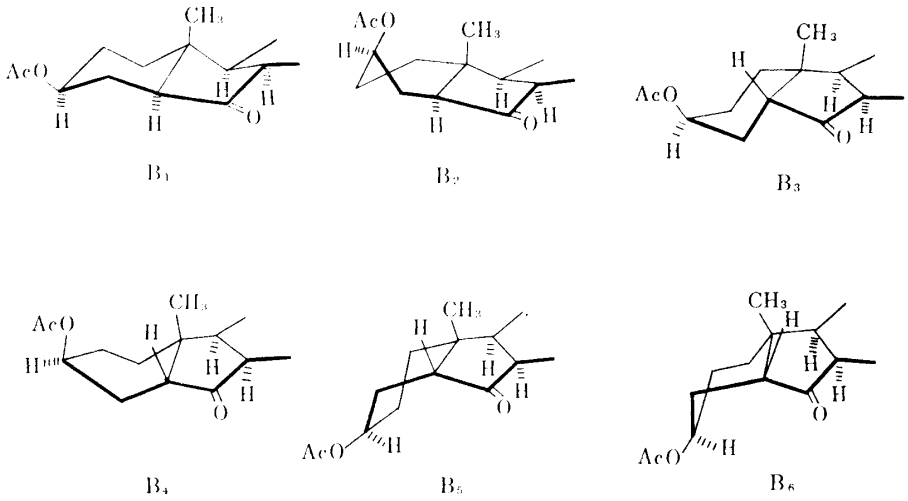

Chart 3.

The isomeric ketol acetate (Ⅳ) resisted reduction either with platinum oxide in acetic acid or sodium borohydride. This observation indicates that the carbonyl group in this compound is sterically hindered. However, Ⅲa and Ⅳa could be reduced with lithium aluminum hydride to yield the same diol (Va), which with a slightly excess amount of chromium trioxide in acetic acid for oxidation of one hydroxyl group yielded C_6-monoketone (Ⅲa), in addition to a small amount of diketone (Ⅵa) and which even with the excess acetic anhydride in pyridine afforded only a 3-mono-acetate (Ⅶa). Oxidation of Ⅶa with chromium trioxide gave the ketol acetate (Ⅳa).

The preferential oxidation and resistance to acetylation of the C_6-hydroxyl group in the diol (Va) suggest that the hydroxyl group is sterically hindered and therefore must have 6β-configuration. The nuclear magnetic resonance data further confirms this assignment: The C_{18}- and C_{19}-methyl proton resonance of the diol (Va) shifts downward by 0.18 and 0.11 p.p.m., respectively, as compared to 3β,6α-diol (Xa), which was obtained in addition to 3β,6β-diol (Ⅺa), from Ia by lithium aluminum hydride reduction. The downfield shifts of the angular methyl protons observed in the diol (Va) must arise from spacial interaction between the C_6-hydroxyl group and angular methyl groups.[6,9] Such an interaction can only be expected from an 8α-configuration and thus the structure, B-nor-5β,8α-cholestane-3β,6β-diol was assigned to Va.

Oxidation of the ketol (Ⅲa) and the diol (Va) with excess chromium trioxide in acetic acid afforded the same 3,6-dione (Ⅵa), and a trione (Ⅵd) was obtained from the ketol (Ⅲc) by the same procedure. The C_{18}-methyl signal of Ⅵa and Ⅵd appeared at a higher field by 0.14 p.p.m. in the cholestane series and by 0.21 p.p.m. in the androstane series as compared to those for the corresponding 8β-H-isomers. This can only be again interpreted as a diamagnetic shift caused by the C_6-carbonyl function at the C_8-α-configuration. Since the C_5-configuration remains unaffected during the oxidation process from Va to Ⅲa, the diketone (Ⅵa, d) might also retain the 5β-configuration and thus possess a *cis*-anti-*cis* configuration. The conversion of the ketone (Ⅵa, d)[1] into the ketone (Ⅷa, d) therefore should involve epimerization only at C_8-position.

Experimental*3

The NMR spectra were taken with a Varian A-60 NMR spectrometer, operating at 60 Mc.p.s. on

*3 All melting points were uncorrected. Rotations were measured in $CHCl_3$ solution at 28°. IR spectra were determined using a Perkin-Elmer Model 21 spectrophotometer.

9) Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto, K. Tsuda: This Bulletin, **10**, 338 (1962).

about 10% solution in $CDCl_3$ containing tetramethylsilane as an internal reference. Chemical shifts are represented on τ-value.

Epimerization of 3β-Acetoxy-B-nor-5β-cholestan-6-one (Ia)——a) A solution of Ia (3.0 g.) in MeOH (120 ml.) mixed with a solution of KOH (1.5 g.) in H_2O (5 ml.) was kept at room temperature for 16 hr. After neutralizing with AcOH, the solution was concentrated into a small volume, diluted with H_2O and extracted with Et_2O. The extract was condensed to afford a syrupy residue, which was chromatographed over neutral alumina (Woelm grade III, 80 g.). The first fraction eluted with hexane-benzene (1:1) and benzene gave 2.65 g. of 3β-hydroxy-B-nor-5β,8α-cholestan-6-one (IIIa), which after recrystallization from MeOH gave needles of m.p. 132°, $[\alpha]_D$ −31°(c=3.820). *Anal.* Calcd. for $C_{26}H_{44}O_2$: C, 80.35; H, 11.41. Found : C, 80.00; H, 11.35. IR ν_{max}^{Nujol} cm^{-1} : 3260 (OH), 1734 (CO), $\nu_{max}^{CCl_4}$ cm^{-1} : 3450 (OH), 1730 (CO). The second product obtained from benzene-Et_2O (8:2) fraction was 0.25 g. of 3β-hydroxy-5β,8β-cholestan-6-one (IIa), which was crystallized from hexane to afford needles of m.p. 125~126°, $[\alpha]_D$ +39.5°(c=2.104). *Anal.* Calcd. for $C_{26}H_{44}O_2$: C, 80.35; H, 11.41. Found : C, 80.35; H, 11.41. IR ν_{max}^{Nujol} cm^{-1} : 3430 (OH), 1730, 1713 (splitted CO), $\nu_{max}^{CCl_4}$ cm^{-1} : 3440 (OH), 1734 (CO).

Each of these epimeric ketols (IIa and IIIa) was treated with Ac_2O and pyridine at room temperature for 15 hr. and worked up in a usual way. IIa gave 3β-acetoxy-B-nor-5β,8β-cholestan-6-one (Ia), m.p. 90°, (from MeOH) which was identified by the comparison of its IR spectrum and the mixed melting point determination with the authentic sample. IIIa afforded 3β-acetoxy-B-nor-5β,8α-cholestan-6-one (IVa) as plates of m.p. 109~110°, $[\alpha]_D$ −41°(c=3.701) after recrystallization from MeOH. *Anal.* Calcd. for $C_{28}H_{46}O_3$: C, 78.09; H, 10.77. Found : C, 78.19; H, 10.72.

b) A solution of Ia (100 mg.) in MeOH (5 ml.) containing conc. HCl (0.5 ml.) was refluxed for 2 hr., diluted with H_2O and extracted with Et_2O. The extract was washed with dil. $NaHCO_3$ solution, H_2O and then dried over Na_2SO_4. Removal of the solvent left a sirup (80 mg.). Crystallization from MeOH gave 3β-hydoxy-B-nor-5β,8α-cholestan-6-one (IIIa), as needles of m.p. 131~132°, $[\alpha]_D$ −31°(c=3.610), which was identical with the product obtained above.

B-nor-5β,8α-cholestane-3,6-dione (VIa)——A solutlon of IIIa (400 mg.) in AcOH (10 ml.) was added to a solution of CrO_3 (85 mg.) in 90% aq. AcOH (5 ml.). The mixture was allowed to stand at room temperature for 4 hr., poured into ice-water and extracted with Et_2O. The extract was washed with 1% aq. $NaHCO_3$ solution, H_2O and dried over Na_2SO_4. The solvent was removed to give a crystalline substance (320 mg.), which was recrystallized from MeOH to afford needles of B-nor-5β,8α-cholestane-3,6-dione (VIa), m.p. 134~135°, $[\alpha]_D$ −56°(c=2.833). (lit.,[2] m.p. 135~137°. $[\alpha]_D$ −61° (c=1.11)). *Anal.* Calcd. for $C_{26}H_{42}O_2$: C, 80.77; H, 10.95. Found : C, 80.55; H, 10.94. IR ν_{max}^{Nujol} cm^{-1} : 1739 (6-CO), 1717 (3-CO), $\nu_{max}^{CCl_4}$ cm^{-1} : 1744 (6-CO), 1725 (3-CO).

Attempted Reduction of 3β-Acetoxy-B-nor-5β,8α-cholestan-6-one (IVa) with $NaBH_4$——A solution of $NaBH_4$ (33 mg.) in EtOH (5 ml.) was added to a solution of 3β-acetoxy-B-nor-5β,8α-cholestan-6-one (IVa; 500 mg.) in EtOH (20 ml.). The mixture was stirred at room temperaturet for 4 hr. The excess reagent was decomposed with AcOH and the mixture was diluted with H_2O and extracted with Et_2O which was worked up as usual. A syrupy substance obtained from the extract was chromatographed over alumina (Woelm grade III; 20 g.). The eluate with hexane-benzene (7:3) afforded the starting material (420 mg.) and the benzene eluate gave 72 mg. of a substance, which after recrystallization from MeOH gave a compound, identical with 3β-hydroxy-B-nor-5β,8α-cholestan-6-one (IIIa) of m.p. 131~132°. The identity was confirmed by the comparison of its IR spectrum and the mixed melting point determination with an authentic specimen.

When the reaction was carried out for 34 hr., there was obtained merely the ketol (IIIa).

B-Nor-5β,8α-cholestane-3β,6β-diol (Va)——a) A solution of IVa (1.4 g.) in Et_2O (100 ml.) was mixed with a suspension of $LiAlH_4$ (0.4 g.) in Et_2O (50 ml.). The mixture was refluxed for 30 hr., and worked up as usual. The resulting sirup (1.4g.) was chromatographed over alumina (Woelm grade III; 40 g.). Benzene and benzene-Et_2O (1:1) fraction afforded B-nor-5β,8α-cholestane-3β,6β-diol (Va; 0.9 g.), which after recrystallization from hexane gave granules of m.p. 153°, $[\alpha]_D$ +20°(c=3.065). *Anal.* Calcd. for $C_{26}H_{46}O_2$: C, 79.94; H, 11.87; O, 8.19. Found : C, 79.74; H, 11.67; O, 8.09. IR $\nu_{max}^{CCl_4}$ cm^{-1} : 3450 (broad, OH).

b) A solution of the ketol (IIIa; 100 mg.) in Et_2O (25 ml.) was refluxed with $LiAlH_4$ (50 mg.) for 30 hr., and worked up as described above. The resulting product (80 mg.) was identified with Va by the comparison of its IR spectrum. Treatment of the diol (Va; 70 mg.) with Ac_2O (3 ml.) and pyridine (5 ml.) gave a monoacetate (VIIa), which failed to crystallize even after chromatography over alumina. *Anal.* Calcd. for $C_{28}H_{48}O_3 \cdot \frac{1}{2}H_2O$: C, 76.75; H, 11.11. Found : C, 76.77; H, 10.97. IR ν_{max}^{Nujol} cm^{-1} : 3570 (OH), 1740, 1250 (OAc).

Oxidation of B-Nor-5β,8α-cholestane-3β,6β-diol 3-Acetate (VIIa)——A solution of VIIa (100 mg.) in AcOH (5 ml.) was treated with an aq. CrO_3 solution (25 mg.) overnight at room temperature and worked up as usual. The product was recrystallized from MeOH to give 43 mg. of 3β-acetoxy-B-nor-5β,8α-cholestan 6-one (IVa), whose infrared spectrum was superimposable with that of the authentic sample.

Oxidation of B-Nor-5β,8α-cholestane-3β,6β-diol (Va)——a) A solution of the diol (Va; 120 mg.) in AcOH (5 ml.) was treated with a solution of CrO_3 (50 mg.) in aq. 80% AcOH (5 ml.) at room temperature for 20 hr. The reaction mixture was poured into ice-water and the product was taken up in Et_2O. The extract was washed with dil. $NaHCO_3$ solution, H_2O and dried over Na_2SO_4. The solvent was removed under a reduced pressure and the residue was crystallized from MeOH to give needles of B-nor-5β,8α-cholestane-3,6-dione (VIa; 97 mg.), m.p. 135~136°, whose IR spectrum was identical in all respects with that of the authentic sample obtained above.

b) To a solution of the diol (Va; 130 mg.) in AcOH (5 ml.) was added a solution of CrO_3 (23 mg.) in aq. 80% AcOH (5 ml.). The mixture was kept at room temperature for 2 hr. and the product was worked up as described above and afforded a syrup (120 mg.), which was chromatographed over alumina (Woelm grade III; 3.5 g.). B-Nor-5β,8α-cholestane-3,6-dione (VIa; 20 mg.) was eluted with hexane-benzene (1:1) and melted at 135~136° after recrystallization from MeOH. The eluate with hexane-benzene (1:2) gave 3β-hydroxy-B-nor-5β,8α-cholestan-6-one (IIIa; 94 mg.), of m.p. 131° (from MeOH). There was observed no depression of melting point on admixture with sample obtained above.

c) A solution of Va (50 mg.) in pyridine (2 ml.) was mixed with a solution of CrO_3 (50 mg.) in pyridine (2 ml.) and the mixture was kept at room temperature for 10 hr. After dilution with H_2O, the product was taken up in Et_2O, the extract was washed consecutively with dil. HCl, dil. $NaHCO_3$ solution and H_2O. Drying over Na_2SO_4 and evaporation of the solvent gave a syrup (50 mg.), which was chromatographed over alumina (Woelm grade III; 3 g.). Hexane-benzene (1:1) fraction gave a diketone (VIa; 20 mg.), m.p. 136° after recrystallization from MeOH. The eluate with hexane-benzene (1:3) afforded the ketol (IIIa; 15 mg.), m.p. 130° (from MeOH). Physical constants of VIa and IIIa were identical with the authentic samples obtained above.

Epimerization of 3β,17β-Diacetoxy-B-nor-5β,8β-androstan-6-one (Ib)——A solution of Ib (2.0 g.) in MeOH (40 ml.) was allowed to stand with a solution of KOH (2.0 g.) in H_2O (2 ml.) at room temperature for 16 hr. After the reaction mixture was acidified with AcOH, the solvent was condensed into a small volume and the residue was diluted with H_2O, shaken with Et_2O. The extract was worked up as usual. The residual solid was recrystallized from AcOEt-hexane to yield needles of 3β,17β-dihydroxy-B-nor-5β,8α-androstan-6-one (IIIc; 1.13 g.), m.p. 178~179°. *Anal.* Calcd. for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.66; H, 9.91. IR ν_{max}^{Nujol} cm^{-1}: 3290 (broad, OH), 1731 (6-CO). The residue (500 mg.) obtained from the mother liquor was acetylated with Ac_2O (1 ml.) in pyridine (5 ml.) and the products were chromatographed over alumina (Woelm grade III; 15 g.). The eluate with hexane-benzene (1:3) gave 3β,17β-diacetoxy-B-nor-5β,8α-androstan-6-one (IVb; 310 mg.), m.p. 164°, $[\alpha]_D$ −85° (c=3.515), as plates after recrystallization from MeOH. *Anal.* Calcd. for $C_{22}H_{32}O_5$: C, 70.18; H, 8.57. Found: C, 69.94; H, 8.56. IR ν_{max}^{Nujol} cm^{-1}: 1736 (broad, 6-CO, 3-OAc, 17-OAc), 1260, 1250, 1032 (OAc). The eluate with benzene gave 26 mg. of 3β,17β-diacetoxy-B-nor-5β,8β-androstan-6-one (Ib), m.p. 105° (from hexane), whose identification was accomplished by the comparison of its IR spectrum with that of the authentic sample obtained above.

B-Nor-5β,8α-androstane-3,6,17-trione (VId)——A solution of IIIc (300 mg.) in AcOH (10 ml.) was treated with CrO_3 (200 mg.) in a few amount of H_2O overnight at room temperature. The excess reagent was decomposed with MeOH and the mixture was diluted with H_2O. The product was taken up with $CHCl_3$, and the extract was worked up as usual. Drying over Na_2SO_4 and evaporation of the solvent yielded a crystalline product (210 mg.). Recrystallization from benzene-hexane gave plates of B-nor-5β,8α-androstane-3,6,17-trione (VId; 155 mg.), m.p. 215~217°, $[\alpha]_D$ −43.6° (c=2.845). *Anal.* Calcd. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.68; H, 8.44. IR ν_{max}^{Nujol} cm^{-1}: 1730 (6-CO, 17-CO), 1705 (3-CO).

B-Nor-5β,8β-androstane-3,6,17-trione (VIIId)——A solution of VId (100 mg.) in MeOH (10 ml.) was set aside with 5% MeOH-KOH (0.3 ml.) at room temperature overnight. After dilution with H_2O, the product was taken up in CH_2Cl_2, the extract was washed with H_2O and dried over Na_2SO_4. The solvent was evaporated and the residue was crystallized from Et_2O gave sticks of B-nor-5β-androstane-3,6,17-trione (VIId; 61 mg.), m.p. 161~162°, $[\alpha]_D$ +20° (c=2.21). (lit.[8] m.p. 162.5~163.5°, $[\alpha]_D^{20}$ +18±1°). *Anal.* Calcd. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.81; H, 8.30. IR ν_{max}^{Nujol} cm^{-1}: 1746~1738 (6-CO, 17-CO), 1715 (3-CO).

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Summary

The structure of a base-induced isomerization product of B-nor-6-oxo-5β-steroid (I) was assigned to be B-nor-6-oxo-5β,8α-steroid (III) and conformation of the A-ring was also discussed on the basis of evidence obtained from nuclear magnetic resonance spectra.

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