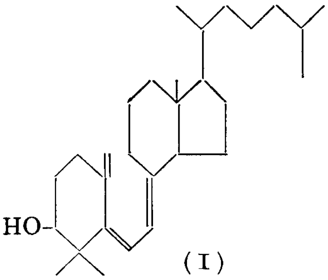
UDC 547.92.07

40. **Eiji Ohki** : Steroid Studies. XVIII.[1] Reduction of 5,7-Diene in 10-Isosteroid.

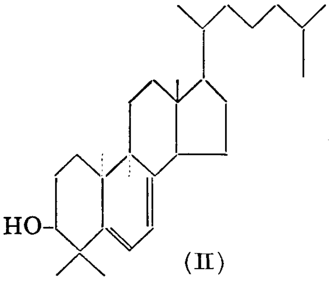
(*Institute of Applied Microbiology,*[*1] *University of Tokyo*)

It had been shown in an earlier work[2] that pyrolysis of 4,4-dimethylcholecalciferol (I), prepared from cholesterol, predominantly gave the pyrocalciferol-type 4,4-dimethyl-10-isocholesta-5,7-dien-3β-ol (II) by the effect of *gem*-dimethyl group in the 4-position. Studies on steroids possessing unnatural configuration like (II) are rather interesting from the point of stereochemistry and many such work have been published.[3] It is now considered that (II) and its derivatives, though lacking methyl group in 14-position, are thought to have a skeleton which is enantiomorphic with the euphol group[4] of triterpenoid, especially with tirucallol (III). It is biogenetically important, therefore, to synthesize isosteroids like (II) and to examine its reactions in order to establish correlation between cholesterol and euphol.

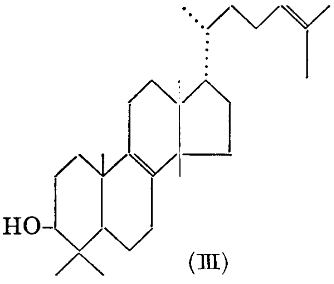
In the present series of work, the behavior of homoannular diene in (II) to reduction was compared with that of natural 10-normal-steroid and examinations were also made on the possibility of preparing the enantiomorph of euphol group from lanosterol.



(I)



(II)



(III)

Reduction of 10-Normal Series

The homoannular 5,7-diene in steroids is reduced by sodium and ethanol to 7-monoene[5] and this metallic reduction was first attempted. In the case of 4,4-dimethyl-7-dehydrocholesterol[6] (IV), as shown in Chart 1, the reduction did not proceed at all and the starting material was recovered. In the case of 4,4-dimethylcholesta-5,7-dien-3-one[6] (V), the ketone group alone underwent reduction to afford (IV) in 70% yield and the diene system was not reduced. This is considered to be due to the steric hindrance of the *gem*-dimethyl group in 4-position which prevented the attack of the reduction agent. In a previous work,[2] the acetate (VI) of (IV) was dehydrogenated with mercuric acetate and the trienol acetate (VII) so formed was saponified to 4,4-dimethylcholesta-

---

[*1] Mukogaoka-Yayoi-cho, Bunkyo-ku, Tokyo (大木英二).

[1] Part XVII. K. Tsuda, R. Hayatsu, Y. Kishida : J. Am. Chem. Soc., **82**, (1960), in press.

[2] E. Ohki : This Bulletin, 8, 47(1960).

[3] (a) 8-Isosteroid — C. Djerassi, W. Frick, G. Rosenkranz, F. Sondeheimer : J. Am. Chem. Soc., **75**, 3496(1953); C. Djerassi, A. J. Mason, A. Segaloff : J. Org. Chem., **21**, 490(1956); C. Djerassi, G. H. Thomas : J. Am. Chem. Soc., **79**, 3835(1957). (b) 9-Isosteroid — P. Bladon, *et al.* : J. Chem. Soc., **1953**, 2921; A. Crawshaw, *et al.* : *Ibid.*, **1955**, 3420. (c) 14-Isosteroid — J. B. Bream, D. C. Eaton, H. B. Henbest : J. Chem. Soc., **1957**, 1974; N. L. Wedler, R. P. Graber : J. Am. Chem. Soc., **79**, 4476(1957).

[4] J. Simonsen, W. C. J. Ross : "The Terpenes," Vol. V (1957). Cambridge University Press. Cf. M. Menard, H. Wyler, A. Hiestand, D. Arigoni, O. Jeger, L. Ruzicka : Helv. Chim. Acta, **38**, 1517(1955); M. C. Dauson, T. G. Halsall, E. R. H. Jones, G. D. Meakins, P. C. Phillips : J. Chem. Soc., **1956**, 3176, and earlier reports.

[5] W. Bergmann, J. A. Klacsmann : J. Org. Chem., **13**, 21(1948), and earlier reports.

[6] F. Gautchi, K. Bloch : J. Biol. Chem., **233**, 1343(1958).

5,7,9(11)-trien-3β-ol (VIII). This trienol (VIII) was submitted to reduction with sodium and ethanol to give a mixture from which, by fractional crystallization, (IV) and a substance (IX) of m.p. 143~145° were obtained. The ultraviolet spectrum of (IX) exhibited absorptions at 238, 243, and 251 mμ, characteristic to heteroannular 7,9(11)-diene. Moreover, its acetate (X) was found to be identical with 4,4-dimethylcholesta-7,9(11)-dien-3β-ol acetate (X), obtained by dehydrogenation of 4,4-dimethylcholest-7-en-3β-ol acetate (XI) with mercuric acetate, and the structure of (IX) was established. It follows, therefore, that reduction of the trienol (VIII) produces a diene mixture of (IV) and (IX).[7]

Bloch and others[6] carried out catalytic reduction of (V) over Raney nickel and obtained 4,4-dimethylcholest-7-en-3β-ol (XII). This reaction was followed and (XII) was produced from (V), but with by-product formation of saturated 4,4-dimethylcholestan-3β-ol (XIII). (VI) and (VII) also formed the acetate (XI) of (XII) in a good yield by this reaction under identical conditions. Consequently, catalytic reduction differs from the use of sodium and ethanol, and the effect of the dimethyl group at 4-position is small, the double bonds at 5- and 9-positions easily submitting to reduction like steroids in general.[8]

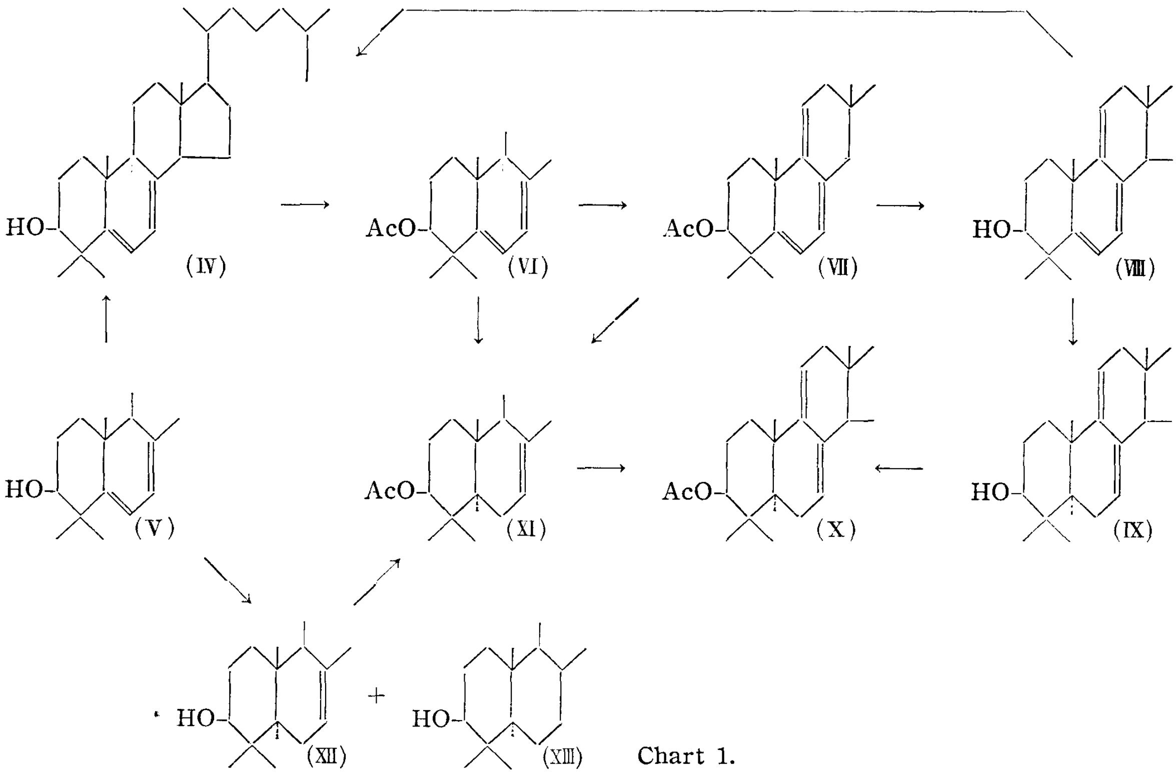


Chart 1.

Reduction of 10-Iso Series

Both 4,4-dimetyl-10-isocholesta-5,7-dien-3β-ol (II) and its 3α-epimer (XIV) are inert to reduction with sodium and ethanol, while 4,4-dimethyl-10-isocholesta-5,7-dien-3-one (XV), obtained by oxidation of (II), forms the alcohol (XIV) and the diene group is not reduced.[2] Since the 5,7-diene double bonds in pyrocalciferol are easily reduced like ergosterol,[9] it is assumed that the dimethyl group in 4-position in 10-isosteroid also prevents reduction of the diene. The trienol acetate (XVII) (the free alcohol of which has not been isolated in crystalline form as yet), obtained by dehydrogenation of the acetate of (II), formed a substance (XVIII) of $C_{25}H_{50}O$, m.p. 84~86°, $[\alpha]_D$ +46.9°, by reduction with

---

[7] Cf. A. Windaus: Ann., **477**, 268(1930).

[8] G.D. Leubach, K.J. Brunings: J. Am. Chem. Soc., **74**, 705(1952).

[9] P. Busse: Z. physiol. Chem., **214**, 211(1933).

sodium and ethanol. The ultraviolet spectrum of (XVIII) did not show any marked absorption in the shorter wave-length region and its infrared spectrum exhibited complicated absorptions in the region of 850~800 cm^{-1}, corresponding to the out-of-plane deformation vibration of a tri-substituted double bond.$^{10)}$ (cf. Fig. 1b). These data and its positive Liebermann-Burchard reaction and tetranitromethane test suggested that (XVIII) is a monoene-alcohol but its structure could not be determined due to lack of the sample. It is considered that while reduction of the trienol (VIII) in the normal series affords a diene mixture, the two double bonds in the trienol (XVII) in the iso series are easily reduced.

Catalytic reduction over Raney nickel was then examined with (XV) and the acetate (XIX) of (XIV). Reduction of (XV) over Raney nickel at elevated temperature afforded a small amount of the ketone (XX), m.p. 100~102°, $C_{29}H_{48}O$, and the alcohol (XXI), m.p. 71~72°, $C_{29}H_{50}O$. (XX) was identified with the ketone obtained by oxidation of (XXI) with chromium trioxide and pyridine. On the other hand, (XIX) over Raney nickel afforded an acetate (XXII), m.p. 137~139°, whose saponification gave the alcohol (XXIII), m.p. 146~148°, $C_{29}H_{50}O$. This alcohol (XXIII) is an isomer of (XXI) and its oxidation with chromium trioxide afforded (XX). It is therefore assumed that (XX), (XXI), and (XXIII) have the same skeleton, except for the substituent at 3-position which is 3-ketone in (XX), 3β-OH in (XXI), and 3α-OH in (XXIII). Both (XXI) and (XXIII) are positive to the Liebermann-Burchard reaction and tetranitromethane test, and their infrared spectra show absorptions corresponding to the tri-substituted double bond$^{10)}$ (cf. Fig. 1c), so that they are monoene-alcohols.

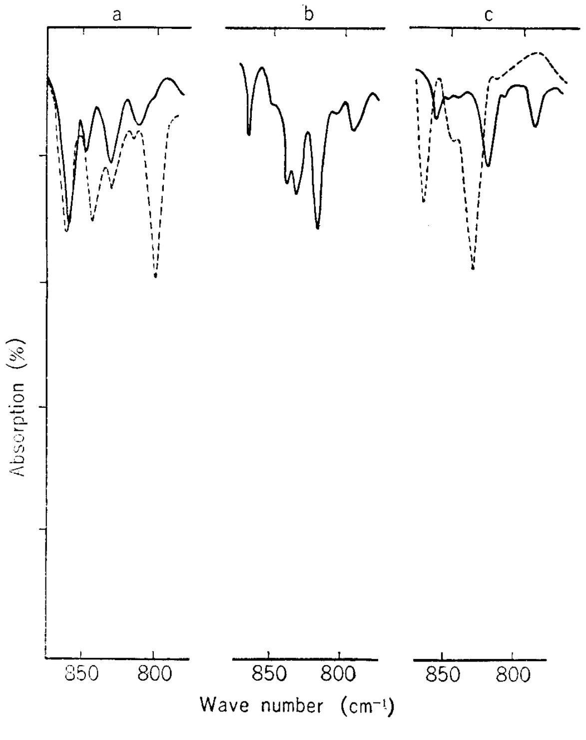


Fig. 1. Infrared Spectra in 870~770 cm^{-1} Region (solids, mulled)

(a) —— 4,4-Dimethylcholest-7-en-3β-ol (XII)
------ 4,4-Dimethylcholest-5-en-3β-ol (XXV)
(b) Reduction product (XVIII) of 4,4-dimethyl-10-isocholesta-5,7,9(11)-trien-3β-ol
(c) ------ 4,4-Dimethyl-10-isocholest-5-en-3α-ol (XXIII)
—— 4,4-Dimethyl-10-isocholest-5-en-3β-ol (XXI)

As a measure for establishing the hydroxyl in 3-position of triterpenoid, there is the dehydration reaction with phosphorus pentachloride. Treatment of (XXIII) having equatorial 3α-hydroxyl with phosphorus pentachloride afforded a dienic hydrocarbon (XXIV), $C_{29}H_{48}$, although it could not be entirely purified to a crystalline form. The ultraviolet spectrum of (XXIV), as shown in Fig. 2, has a broad absorption (ε 9600) in the region of 246~250 mμ. Treatment of 4,4-dimethylcholest-5-en-3β-ol (XXV) with phos-

---

10) P. Bladon, T. M. Fabian, H. B. Henbest, H. P. Koch, G. W. Wood : J. Chem. Soc., **1951**, 2403.

phorus pentachloride according to the method of Hadded and Summers[11] gave a conjugated diene (XXVI) (UV λ_{max} 244~251 mμ (ε 11700)) and its ultraviolet spectrum approximately agreed with that of (XXIV).

On the other hand, treatment of (XXI) possessing an axial hydroxyl in 3-position yielded a hydrocarbon, $C_{29}H_{48}$, whose infrared spectrum exhibited a strong absorption at 728 cm^{-1} for *cis*-ethylene center,[12] and the structure (XXVIII) was assumed for it. Since the same absorption band was also observed in the infrared spectrum of (XXIV) and the ultraviolet spectrum of (XXVII) has only a weak absorption in the shorter wave-length region, as indicated in Fig. 2, there is mutual contamination of (XXIV) and (XXVII) in the dehydration products of (XXI) and (XXIII) in ionic dehydration. The formation of (XXIV) from (XXIII) suggests that the double bond in the monoene-alcohols (XXI and XXIII) formed by reduction over Raney nickel is present in the 5-position (see Chart 2). Consequently, there seems to be little steric hindrance in the double bond at 7—8 position in catalytic reduction of the iso series.

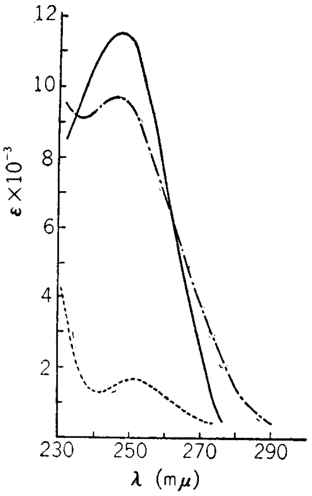


Fig. 2. Ultraviolet Absorption Spectra of Dehydration Products (in MeOH)

------- (XXIV) from (XXIII)
········ (XXVII) from (XXI)
——— (XXVI) from (XXV)

(XXV) was prepared by the method of Hadder and Summers,[10] prisms, m.p. 74~80° (from MeOH).

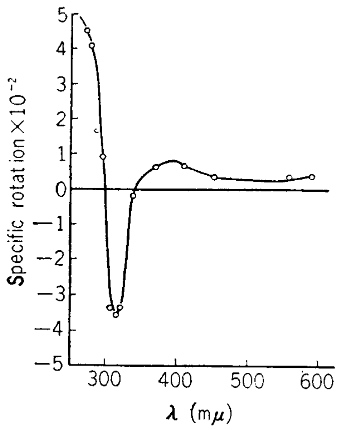


Fig. 3. Optical Rotatory Dispersion Curve of (XX) (in MeOH soln.)

The rotatory dispersion curve of (XX) is indicated in Fig. 3. It is a positive plain curve sharply superimposed with a negative Cotton effect and (XX) is considered to be the mirror image of 4,4-dimethylcholest-5-en-3-one (XXVIII). It was also observed that (XX) corresponds to the rotatory dispersion curve of alunus-5-en-3-one (XXIX).[13]

As shown above, the double bond at 7-position of 9α,10β-steroid resists reduction while that in 9β,10β-steroid was reported to be easily reduced.[3b)],[*2] According to the foregoing experiments, the double bond in 7-position of 9α,10α-steroid is easily reduced and the steric hindrance at 7-position is not necessarily intrinsic to the conformation at 9-

---

[*2] The double bond at 7 in butyrospermol, corresponding to 9β,10α-conformation, is not reduced (I. Heilbron, E. R. H. Jones, P. A. Robins : J. Chem. Soc., **1949**, 444). There is no data on the reduction of euph-7-en-ol, corresponding to the 9α,10β-steroid (D. H. R. Barton, J. F. McGhie, M. K. Pradhan : J. Chem. Soc., **1955**, 876).

11) Y. M. Y. Hadded, G. H. R. Summers : J. Chem. Soc., **1959**, 769.
12) H. B. Henbest, G. D. Meakins, G. W. Wood : *Ibid.*, **1954**, 800.
13) C. Djerassi, O. Halpern, V. Halpern, B. Riniker : J. Am. Chem. Soc., **80**, 4001(1958).

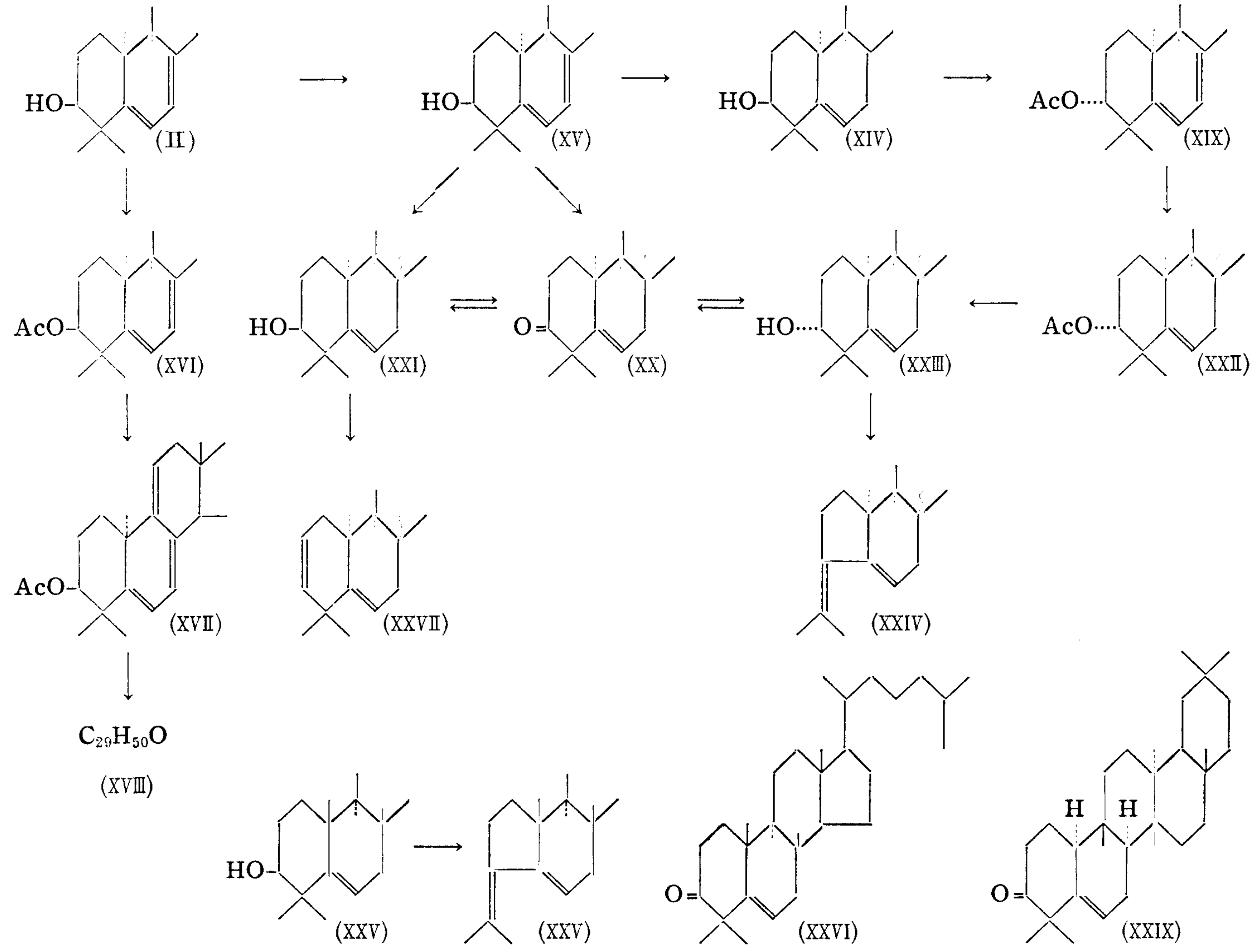


Chart 2.

position but is due to the effect of the whole molecule.[3c)] The conformation at 8-position in (XXI) and (XXⅢ) is now under examination.

Reduction of the ketone group in 3-position in steroids of iso series offered a new observation. Reduction of (XX) with sodium and ethanol produces an equatorial 3α-OH (XXⅢ) while its reduction with lithium aluminium hydride gave (XXI). Formation of (XXI) from (XV) shows that axial 3β-OH (XXI) predominates also in catalytic reduction. In the reaction of natural 10-normal triterpenoids, the ketone at 3-position predominantly produces equatorial 3β-OH by catalytic reduction or reduction with lithium aluminium hydride or sodium and ethanol, while the ketone in the 10-iso series forms two kinds of hydroxyl epimer by these reagents. This fact is in good correspondence with the fact that the mode of reduction of the ketone group in 9-isosteroid differs from that of 9-normalsteroid.[3b)]

Experimental

All melting points are uncorrected. Rotations were determined in $CHCl_3$ and ultraviolet spectra in MeOH. The infrared spectra of all compounds were recorded and were in agreement with the reported structures. Analytical samples were dried for 15 hr. at room temperature in high vacuum.

Metallic Reduction of 4,4-Dimethylcholesta-5,7-dien-3-one (V)—To a solution containing 0.9 g. of (V), m.p. 158~160°, $[\alpha]_D^{10}$ −15°, in 150 cc. of dehyd. EtOH, 6 g. of Na was added in small portions under vigorous boiling. After all the Na had completely dissolved, the reduction mixture was diluted with water and extracted with ether. The extract was washed with water, dried over Na_2SO_4, and evaporated to leave a crystalline mass of 4,4-dimethylcholesta-5,7-dien-3β-ol (VI) which was recrystallized from EtOH to prisms, m.p. 139~140°, $[\alpha]_D^{11}$ −161°(c=1.2). Yield, 0.66 g. The mixed m.p.

and infrared spectrum of the product were identical with those of an authentic sample of (VI).

Metallic Reduction of 4,4-Dimethylcholesta-5,7,9(11)-trien-3β-ol (VIII)—Metallic reduction of 0.3 g. of (VIII), m.p. 128~130°, $[\alpha]_D$ −156°, in the manner described afforded a reduction mixture which, after several recrystallizations from ether-MeOH, gave 4,4-dimethylcholesta-7,9(11)-dien-3β-ol (IX) as needles, m.p. 143~145°. *Anal.* Calcd. for $C_{29}H_{48}O \cdot \frac{1}{4}H_2O$: C, 83.55; H, 11.64. Found : C, 83.42; H, 11.78. UV λ_{max} mμ(ε): 238 (8800), 243 (9500), 251 (6000).

Acetylation of (IX) with pyridine-Ac_2O in the usual manner afforded a crystalline mass which was recrystallized from MeOH to (X) as plates, m.p. 126~128°, $[\alpha]_D^{10}$ +49.3°(c=1.5). *Anal.* Calcd. for $C_{31}H_{50}O_2$: C, 81.88; H, 11.08. Found : C, 81.94; H, 11.10. UV λ_{max} mμ(ε): 236 (8300), 243 (9600), 251 (6000).

The mother liquor of recrystallization of (IX) was concentrated and upon cooling, provided a crystalline mass which, after several recrystallization from MeOH, gave (IV) as prisms, m.p. 138~139°, $[\alpha]_D^{10}$ −150.1 (c=0.5). UV λ_{max} mμ(ε): 272 (10000), 284 (10100), 295(infl.). Identity was proved by infrared spectral comparison with an authentic sample of (IV).

Catalytic Reduction of (V), (VI), and (VII)—A solution of 0.5 g. of (V), m.p. 158~160°, $[\alpha]_D$ −20°, dissolved in 50 cc. of dehyd. EtOH was shaken with 0.5 g. of freshly prepared Raney nickel catalyst (W-2) at 50° and at 200 lb./in² pressure of H_2 for 20 hr. After removal of the catalyst and evaporation of the solvent, the solid residue, which showed no diene absorption in the ultraviolet region, was recrystallized from MeOH to afford 4,4-dimethylcholest-7-en-3β-ol (XII) as needles, m.p. 136~138°,[*3] $[\alpha]_D^{15}$ +11.20°(c=2.9). Yield, 0.30 g.

The acetate (XI) of (XII) was prepared with Ac_2O-pyridine and recrystallized from AcOEt-EtOH as plates, m.p. 138~140°,[*3] $[\alpha]_D^{15}$ +19.6°(c=1.1). *Anal.* Calcd. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48. Found: C, 81.88; H, 11.08.

Hydrogenation of (VI), m.p. 149~151°, $[\alpha]_D$ −101°, or (VII) at elevated temperature with Raney nickel catalyst as described for the reduction of (V) and recrystallization from EtOH afforded (XI) in a good yield. The mixed m.p. and infrared spectra of the product were identical with those of an authentic sample of (XI).

4,4-Dimethylcholesta-7,9(11)-dien-3β-ol Acetate (X)—A solution of 0.7 g. of $Hg(AcO)_2$ in hot AcOH was added over a period of 12 min. to a boiling solution of 0.35 g. of (XI) in 10 cc. of dioxane. Precipitation of HgOAc commenced within 5 min. and the reaction mixture was stirred at room temperature over night. The precipitate of HgOAc was collected and washed consecutively with water, MeOH, and ether. The combined filtrate and washings was washed with 5% H_2SO_4, dil. $NaHCO_3$, and water, dried over Na_2SO_4, and evaporated. The oily residue was dissolved in benzene and the solution was passed through 3 g. of alumina. Elution with the same solvent and recrystallization from MeOH afforded 0.26 g. of (X) as plates, m.p. 126~128°, $[\alpha]_D^{15}$ +48.5°(c=1.1). The mixed m.p. and infrared spectrum of the product were identical with those of an authentic sample of (X) obtained by metallic reduction of (VIII), following acetylation.

Metallic Reduction of 4,4-Dimethyl-10-isocholesta-5,7,9(11)-trien-3β-ol Acetate (XVII)—Metallic reduction of 0.2 g. of (XVII), m.p. 131~133°, $[\alpha]_D$ −42.6°, with Na in EtOH, in the manner described for the reduction of (V), afforded a crystalline mass which recrystallized from MeOH to needles (XVIII), m.p. 84~85°, $[\alpha]_D$ +46.9°(c=1.5). *Anal.* Calcd. for $C_{29}H_{50}O \cdot \frac{1}{4}H_2O$: C, 83.08; H, 12.14. Found: C, 82.72; H, 11.72. Coloration to Lieberman-Burchard and tetranitromethane test was positive. The acetate of (XVIII) was prepared with Ac_2O-pyridine, but its crystallization was unsuccessful.

Catalytic Reduction of 4,4-Dimethyl-10-isocholesta-5,7-dien-3-one (XV)—i) Preparation of 4,4-Dimethyl-10-iso-8ξ-cholest-5-en-3-one (XX) : A solution of (XV), m.p. 89~91°, $[\alpha]_D$ +493°, dissolved in 15 cc. of dehyd. EtOH was shaken with 0.5 g. of freshly prepared Raney Ni catalyst at 50° and at 400 lb./in² H_2 pressure for 15 hr. After removal of the catalyst and evaporation of the solvent, the oily residue, which showed no diene absorption in the ultraviolet region, was chromatographed over 30 g. of alumina. The fraction (0.2 g.) eluted with petr. ether (b.p. 45~60°) was recrystallized from MeOH to (XX) as prisms, m.p. 100~102°, $[\alpha]_D^{10}$ +28.28°(c=2.2). *Anal.* Calcd. for $C_{29}H_{48}O$: C, 84.40; H, 11.72. Found : C, 84.07; H, 11.50. R.D. (c=0.9 in MeOH) at 26.1° : $[\alpha]_D$ +33.3°, $[\alpha]_{546}$ +31.1°, $[\alpha]_{436}$ +44.4°, $[\alpha]_{405}$ +58.0°, $[\alpha]_{366}$ +51.1°, $[\alpha]_{336}$ −5.6°, $[\alpha]_{319}$ −335.6°, $[\alpha]_{313}$ −363.2°, $[\alpha]_{310}$ −355.6°, $[\alpha]_{302}$ −83.6°, $[\alpha]_{297}$ +65.5°, $[\alpha]_{275}$ +420°, $[\alpha]_{265}$ +451°. UV : λ_{max} 291 mμ(ε=330).
ii) Preparation of 4,4-Dimethyl-10-iso-8ξ-cholest-5-en-3β-ol (XXI) : The fractions (0.4 g.) eluted with petr. ether-benzene (8:2, 1:1) were recrystallized from MeOH-ether to (XXI) as needles, m.p. 71~72°, $[\alpha]_D^{16}$ +101.2°(c=2.5). Coloration to Lieberman-Burchard and tetranitromethane tests was positive. *Anal.* Calcd. for $C_{29}H_{50}O$: C, 83.99; H, 12.15. Found : C, 84.08; H, 12.04.

The acetate of (XXI) was prepared with Ac_2O-pyridine in the usual manner and recrystallized from EtOH as needles, m.p. 114~115°, $[\alpha]_D^{16}$ +104.1°(c=2.1). *Anal.* Calcd. for $C_{31}H_{52}O_2$: C, 81.52;

[*3] Gautchi and Bloch[6] gives for (XII) m.p. 145~147°, $[\alpha]_D$ +5°, and for (XI), m.p. 134~136°, $[\alpha]_D$ +25°.

H, 11.48. Found : C, 81.75; H, 11.39.

To a stirred solution of 0.5 g. of CrO_3 in 30 cc. of pyridine, 0.2 g. of (XXI) dissolved in 10 cc. of pyridine was added at 0° and allowed to stand at room temperature over night. After dilution with ether and filtration of the precipitate, the filtrate was diluted with water and extracted with ether. The extract was washed with dil. HCl, $NaHCO_3$, and water, dried over Na_2SO_4, and evaporated *in vacuo* to leave a crystalline mass of (XX) which was recrystallized from MeOH; m.p. 100～102°, $[\alpha]^{11}_{D}$ +22.6° (c=1.0). The mixed m.p. and infrared spectrum of the product were identical with those of an authentic sample of (XX).

Catalytic Reduction of 4,4-Dimethyl-10-isocholesta-5,7-dien-3*α*-ol Acetate (XIX)—Hydrogenation of (XIX), m.p. 97～98°, at elevated temperature with Raney Ni catalyst as described for the reduction of (XV) afforded a crystalline mass which was recrystallized from EtOH to (XXII) as plates, m.p. 137～139°, $[\alpha]^{13}_{D}$ +44.6° (c=2.2). *Anal.* Calcd. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48. Found : C, 81.81; H, 11.59.

Saponification of (XXII) with MeOH-KOH afforded a free alcohol (XXIII) as granular prisms, m.p. 146～148°, $[\alpha]^{18}_{D}$ +59.3° (c=2.3). *Anal.* Calcd. for $C_{29}H_{50}O$: C, 83.99; H, 12.15. Found : C, 83.76; H, 12.08. Coloration to Lieberman-Burchard and tetranitromethane tests was positive.

Oxidation of (XXIII) with CrO_3-pyridine in the manner as described for (XXI) → (XX) afforded a crystalline mass of (XX) which was purified by chromatography and recrystallization. The mixed m.p. and infrared spectrum of the product were identical with those of an authentic sample of (XX).

Reduction of (XX)—i) Reduction of 0.3 g. of (XX) with Na in EtOH in the manner described for the reduction of (V) afforded a crystalline mass which was recrystallized from MeOH and identified with an authentic sample of (XXIII) by its infrared spectrum and mixed m.p. Yield, 0.13 g.

ii) A mixture of 20 cc. of ether containing 25 mg. of (XX) and 0.1 g. of $LiAlH_4$ was allowed to reflux for 2 hr., after which the excess hydride was decomposed with a few drops of water. Following addition of dil. HCl (5 cc.), the mixture was extracted with ether, the extract was washed with water, dried over Na_2SO_4, and evaporated. The crystalline residue was recrystallized from MeOH to (XXI) as prisms, m.p. 71～72°. The mixed m.p. and infrared spectrum of the product were identical with those of an authentic sample of (XXI).

Dehydration of (XXIII) and (XXI) with PCl_5—i) A solution of 0.2 g. of (XXIII) in 30 cc. of hexane was shaken for 1 hr. with 0.5 g. of PCl_5. Filtration of the solution through alumina gave an oil which was negative to Beilstein test for halogen. Analytical samples were prepared by distillation in high vacuum (oil bath temp. 180～200°). Yield, 36 mg. *Anal.* Calcd. for $C_{29}H_{48}$: C, 87.80; H, 12.20. Found : C, 87.95; H, 12.24.

ii) Dehydration of 0.2 g. of (XXI) with PCl_5 in hexane in the manner described for (XXIII) afforded an oily product. Yield, 40 mg. *Anal.* Calcd. for $C_{29}H_{46}$: C, 87.80; H, 12.20. Found : C, 87.05; H, 12.11.

The author expresses his deep gratitude to Prof. K. Tsuda of this Institute. He is indebted to Prof. Y. Hirata and Mr. S. Yamamura of the University of Nagoya for their cooperation in the measurement of rotatory dispersion curves, to Misses H. Yamanouchi and K. Hayashi for elementary analyses, and to Miss N. Kurosawa for infrared spectral measurements.

Summary

The behavior of the double bond in the various derivatives of 4,4-dimethyl-10-isocholesta-5,7-dien-3*β*-ol (II) to reduction with sodium and ethanol or over Raney nickel catalyst was comparatively examined with that of 10-normal steroid. It was thereby found that the double bond at 7-position in the iso series is easily reduced by catalytic reduction over Raney nickel.

(Received August 6, 1959)