

**Studies on Conformation and Reactivity. VI.<sup>1)</sup> The Reduction Reaction  
of Cholesta-3,5-dieno[3,4-*b*]oxathiane with Lithium in Liquid  
Ammonia. The Characterization of Unique Ultraviolet  
Absorption of the 3,5-Dieno[3,4-*b*]oxathiano System<sup>2)</sup>**

AKIHIKO ISHIDA, YOSHIRO HIYOSHI, TOSHITAKA KOGA,  
and MUNEMITSU TOMOEDA

*Faculty of Pharmaceutical Sciences, Kanazawa University<sup>3)</sup>*

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In connection with characterization of unique ultraviolet absorptions at around 223 and 270  $m\mu$  of the 3,5-dieno[3,4-*b*]oxathiano system in the steroid nucleus, cholesta-3,5-dieno[3,4-*b*]oxathiane was reduced with lithium in liquid ammonia to give cholest-3-eno[3,4-*b*]oxathiane accompanied by 4 $\alpha$ -( $\beta$ -hydroxyethylthio)-cholest-5-ene, bis(cholest-4-en-4-yl)disulfide, and a mixture of cholest-4-ene and -5-ene. The 3-eno[3,4-*b*]oxathiano system thus obtained gave in its ultraviolet spectrum an absorption at 227  $m\mu$ . It led to a conclusion that the local conjugation of non-bonding *p*-electrons of oxygen and sulfur atoms and  $\pi$  electrons of 3-C and 4-C atoms in the conformationally rather fixed 3-eno[3,4-*b*]oxathiano system affords a unique ultraviolet absorption in a shorter wave length region than 230  $m\mu$ . Origin of characteristic ultraviolet absorptions of the 3,5-dieno[3,4-*b*]dithiano system was analogously deduced.

In the previous papers of this series,<sup>4-7)</sup> we have dealt with the unique ultraviolet absorption spectra of the 3,5-dieno[3,4-*b*]oxathiano (I) and its dithiano (II) systems of the cholestane, 17 $\beta$ -acetoxyandrostane, 16 $\alpha$ ,17 $\alpha$ -epoxy-20-oxopregnane, and 17 $\alpha$ -hydroxy-20-oxopregnane series. The oxathiano (I) and dithiano (II) systems exhibited two strong bands at around 223 and 270  $m\mu$ , and around 240 and 292  $m\mu$ , respectively. Fieser, *et al.*<sup>8)</sup> have suggested that origin of the second bands appearing in the longer wave region can be attributed to the 4-thio(III) and 3,4-dithio (IV) substituted 3,5-dienochromophores. Characteriza-

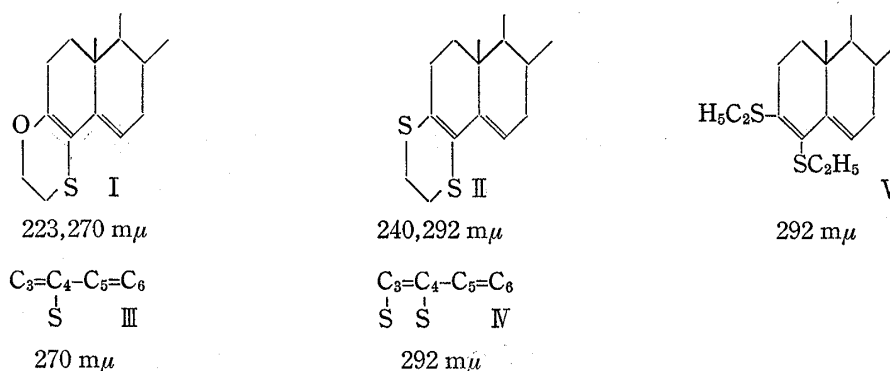


Chart 1

- 1) The Part V: M. Tomoeda, M. Inuzuka, P. Furuta, and M. Shinozuka, *Tetrahedron*, **24**, 959 (1968).
- 2) Presented at the Annual Meeting of the Pharmaceutical Society of Japan, Sendai, October 1966.
- 3) Location: *Takara-machi, Kanazawa*.
- 4) M. Tomoeda, M. Ishizaki, H. Kobayashi, S. Kanatomo, T. Koga, M. Inuzuka, and T. Furuta, *Tetrahedron*, **21**, 733 (1965).
- 5) M. Tomoeda, M. Inuzuka, T. Furuta, and T. Koga, *Chem. Pharm. Bull.* (Tokyo), **13**, 769 (1965).
- 6) M. Tomoeda, T. Furuta, and T. Koga, *Chem. Pharm. Bull.* (Tokyo), **13**, 1078 (1965).
- 7) M. Tomoeda, A. Ishida, and T. Koga, *Chem. Pharm. Bull.* (Tokyo), **15**, 887 (1967).
- 8) L.F. Fieser, C. Yuan, and T. Goto, *J. Am. Chem. Soc.*, **82**, 1966 (1960).

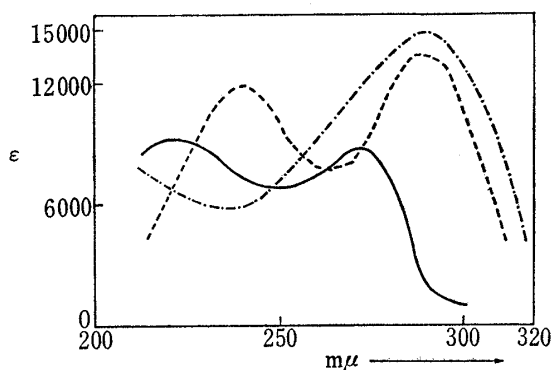


Fig. 1. The UV Absorption Curves (in *n*-Hexane) of — 3,5-Dieno[3,4-*b*]oxathiano (I), ---- 3,5-Dieno[3,4-*b*]dithiano (II), and -·-·- 3,5-Dieno-3,4-bis(ethylthio)(V) Systems in the Cholestane Series

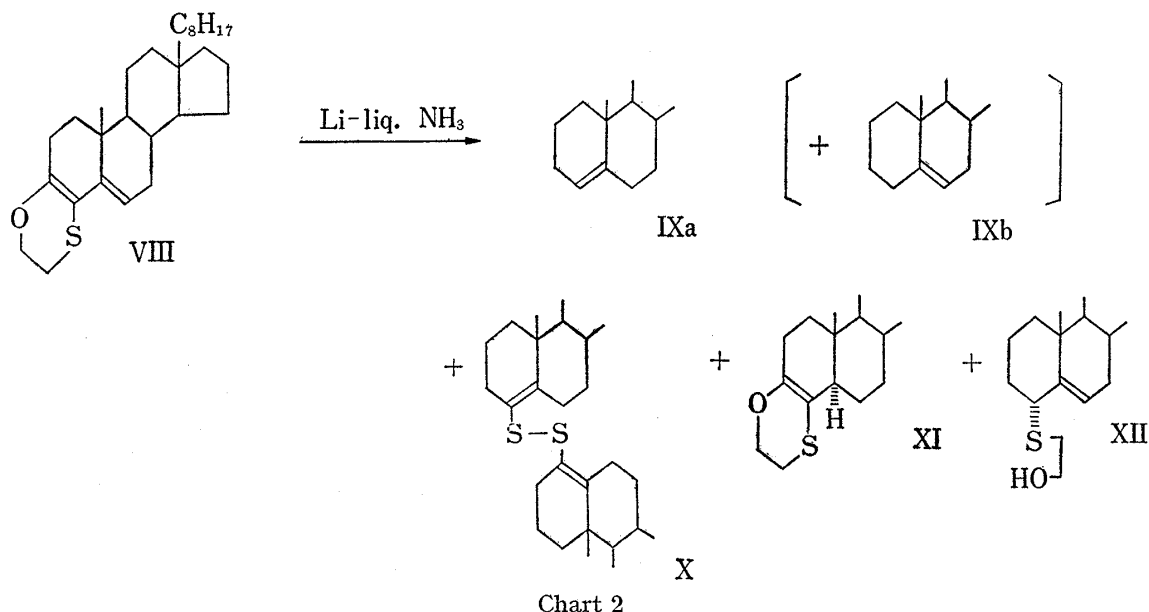
tion of the remaining absorption bends in the shorter wave length region, *i.e.* around 223  $m\mu$  for I and around 240  $m\mu$  for II, has however remained unsolved.

In view of the fact that the 3,4-bis-(ethylthio)-substituted 3,5-dieno (V) system of the cholestane and other steroid series in which the ethylthio group may rotate freely, exhibited only one strong band at around 292  $m\mu$ , which corresponds to the second absorption band at the longer wave length region of II, we have tentatively assigned the first bands of I and II to be attributable to the local conjugation of non-bonding *p*-electrons of sulfur and oxygen atoms and  $\pi$  electrons of 3-C and 4-C atoms in the conforma-

tionally rather fixed oxathiano (I) and dithiano (II) systems possibly in a half-chair conformation.

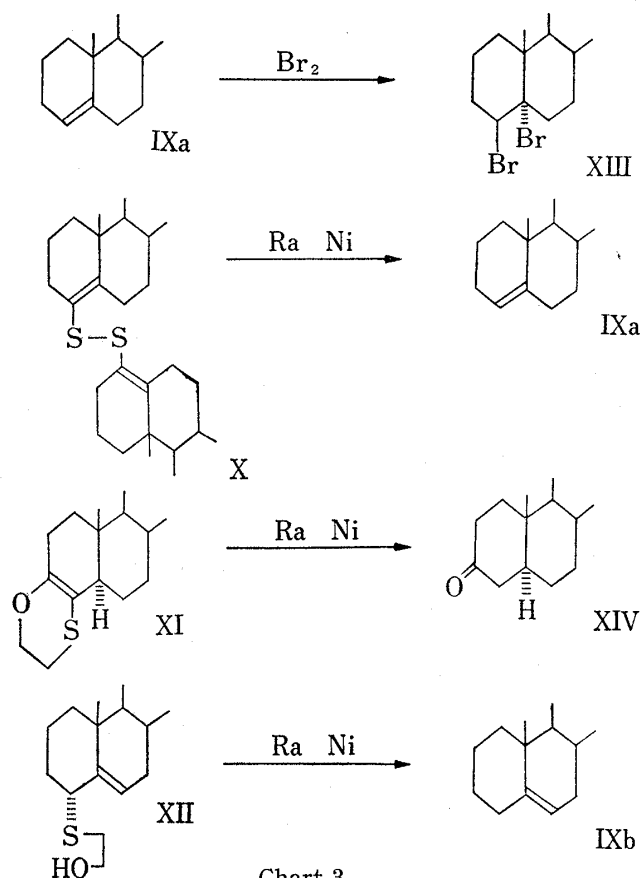
For confirmation of our tentative assignment for the origin of ultraviolet (UV) absorption of the systems I and II, it appeared to be desirable to synthesize 3-eno[3,4-*b*]oxathiane (VI) or its dithiano (VII) systems and examine their UV informations. Furthermore, these systems, VI and VII, together with I and II, appeared to be attractive as starting material for photoinduced reactions. The present paper deals with the reduction reaction of cholesta-3,5-dieno-[3,4-*b*]oxathiane (VIII)<sup>4</sup> with lithium in liquid ammonia leading to the formation of the desired 3-eno[3,4-*b*]oxathiano system, its spectral analysis, and proof for our UV spectral assignment in question. Photochemical behavior of the 3,5-dieno[3,4-*b*]oxathiano (I) and 3-eno[3,4-*b*]oxathiano (VI) systems will be reported elsewhere.

Reduction of VIII with an excess amount of lithium in liquid ammonia was carried out according to the procedure of Takeda, *et al.*<sup>9</sup> with slight modification. After usual work up of the reaction mixture, the crude solid product with the UV absorption maxima at 224 and 227  $m\mu$  was subjected to column chromatography over silica gel to give four crystalline products, IX—XII.



9) K. Takeda, T. Komeno, N. Tokutake, and Y. Kanematsu, *Chem. Pharm. Bull.* (Tokyo), **18**, 905 (1964).

The product (IX) eluted from the chromatogram with petroleum ether as eluent was first an amorphous solid of mp 59—62°,  $[\alpha]_D +24^\circ$ . Its infrared (IR) spectrum showed an absorption at 1663  $\text{cm}^{-1}$  attributable to a double bond. The nuclear magnetic resonance (NMR) spectrum exhibited a peak at  $\tau$  4.72 (one proton, broad). Added to these evidence, the NMR information about 19-methyl group, a peak at  $\tau$  8.99, suggested that a tri-substituted double bond exists in the product IX probably at 4 or 5 position.<sup>10</sup> Rechromatography followed by recrystallization from acetone afforded colorless needles (IXa), which gave mp 73—75°,  $[\alpha]_D +48^\circ$ , and was proved to be cholest-4-ene<sup>11</sup> (yield 5.1%) by microanalysis and by mixed mp determination. All the physical properties of the needles (IXa) corresponded well to those of its authentic specimen. The structure of IXa was further proved that IXa was brominated in carbon tetrachloride to give the corresponding dibromide (XIII) in a high yield which was proved to be identical with its authentic specimen<sup>11</sup> derived from cholest-4-ene. It is therefore concluded that the crude product IX consists mainly from the 4-ene (IXa) probably contaminated with cholest-5-ene (IXb) which affected physical constants of the major product IXa little.



The product X eluted second from the chromatogram with petroleum ether as eluent was obtained, after rechromatography over silica gel, as colorless needles of mp 193—194°,  $[\alpha]_D +70^\circ$ . The microanalysis of the compound suggested the molecular formula to be  $(\text{C}_{29}\text{H}_{45}\text{S})_n$ . The Mass spectrum showed its  $\text{M}^+$  peak at 802, and the molecular formula was therefore confirmed to be  $(\text{C}_{29}\text{H}_{45}\text{S})_2$ . The yield of X was then calculated to be 8.1%. The UV spectrum exhibited an absorption at 224  $\text{m}\mu$  ( $\epsilon$ , 19800) which suggested presence of a chromophore probably containing a sulfide or disulfide function<sup>12</sup> conjugated with double bond enhancing delocalization of  $p$ -electron system of the sulfide function. Presence of the disulfide function was proved by the Mass spectrum which showed fragment peaks at 401 and 369 which corresponded to  $\text{C}_{29}\text{H}_{45}\text{S}$  and  $\text{C}_{29}\text{H}_{45}$  respectively. The IR spectrum with an absorption at 1610  $\text{cm}^{-1}$  suggested presence of a double bond, however, presence of vinylic hydrogen was excluded NMR spectroscopically. The NMR spectrum also exhibited the 19-methyl peak<sup>10</sup> at  $\tau$  8.98 and the doublet  $6\alpha$ -hydrogen peak at  $\tau$  6.71 ( $J=14.5$  cps)<sup>13</sup> which supported the position of the double bond in the compound to be 4. All these evidence supported the struc-

10) N.S. Bhacca and D.H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day Inc., San Francisco, 1964, p. 13.

11) J. Broome, B.R. Brown, A. Robestes, and A.M.S. White, *J. Chem. Soc.*, **1960**, 1406.

12) A.E. Gillam and E.S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," E.J. Arnold (E.J.) and Son, Ltd., London, 1960, p. 69.

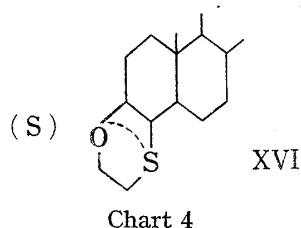
13) For assignment of the peak by  $6\alpha$ -hydrogen under a deshielding effect of the 4-thio-substituted 4-ene system, see ref. 14.

ture of the product X to be bis(cholest-4-en-4-yl)disulfide. The structure was further supported by chemical evidence that desulfurization of X with Raney Ni gave cholest-4-ene (IXa)<sup>11</sup> in a high yield.

The product XI eluted third from the chromatogram with 4:1 petroleum ether-benzene as eluent was obtained as colorless needles of mp 191–192°,  $[\alpha]_D -27^\circ$ . The microanalysis suggested the molecular formula to be  $C_{29}H_{48}OS$ . The yield was then calculated to be 13.9%. The UV spectrum showed an absorption at 227 m $\mu$  ( $\epsilon$ , 4900), and the IR spectrum a rather strong absorption at 1648  $cm^{-1}$ . It was suggested from these evidence that there might be a chromophore with sulfide function conjugated to double bond.<sup>12</sup> Presence of vinylic hydrogens was excluded by the NMR spectrum which, on the other hand, exhibited peaks at  $\tau$  5.53–6.17 (multiplet),  $\tau$  6.99–7.16 (multiplet), and  $\tau$  9.14 (singlet) assignable to  $-O-CH_2-$ ,  $-S-CH_2-$ , and 19-methyl groups in the compound respectively. Furthermore, the fact that the peak due to 19-methyl group appeared at such a high field as  $\tau$  9.14 clearly suggested the position of the double bond to be 3 and not 4 or 5.<sup>10</sup> It could thus be concluded that the product XI is [3,4-*b*]oxathiano-5 $\alpha$ -cholest-3-ene formed as a result of reduction of the double bond at 5 position from the  $\alpha$ -side without any reductive cleavage of the oxathiano ring. The structure of XI was further proved chemically that desulfurization of XI with deactivated Raney Ni gave cholestan-3-one (XIV) in a fairly good yield.

The fourth product XII eluted from the chromatogram with benzene as eluent was obtained as colorless needles of mp 108–109°,  $[\alpha]_D -16^\circ$ . The microanalysis corresponded to the molecular formula of  $C_{29}H_{50}OS$ , and the yield was calculated to be 14.7%. The IR spectrum showed an absorption at 3256  $cm^{-1}$  due to hydroxyl group, and the NMR spectrum exhibited triplets ( $J=6$  cps) at  $\tau$  6.32 (two protons) and  $\tau$  7.31 (two protons) which could be assigned to  $-O-CH_2-$  and  $-S-CH_2-$  groups respectively. The  $-O-CH_2-$  and  $-S-CH_2-$  groups in the conformationally rather fixed oxathiano ring so far examined gave multiplets and not triplets.<sup>4-7</sup> It was therefore deduced that hydrogenolysis of C<sub>3</sub>-O bond took place to give a free-rotating  $-S-CH_2-CH_2-OH$  group at 4-position. The IR spectrum also showed an absorption at 1658  $cm^{-1}$  due to double bond, and the NMR spectrum exhibited a vinylic proton peak at  $\tau$  4.12. Furthermore the NMR spectrum exhibited a peak due to 19-methyl group at  $\tau$  9.01 which suggested the position of a double bond in the compound to be 4 or 5 and not 3.<sup>10</sup> The NMR spectrum also exhibited a broad doublet at  $\tau$  6.56 with a large  $J$  of 12 cps, which suggested that the peak could be assigned to hydrogen of  $>C_4H-S-$  group, and that the configuration of 4-H is axial type or  $\beta$  and then that of 4- $SCH_2CH_2OH$  group, equatorial type or  $\alpha$ . All these evidence supported the structure of XII to be 4 $\alpha$ -( $\beta$ -hydroxyethylthio)cholest-5-ene. Another evidence for the structure was provided chemically that XII afforded, on acetylation with acetic anhydride-pyridine, the corresponding acetate (XV). All the physical properties of the acetate (XV) were proved to support its structure. Another chemical evidence for the structure of XII was that desulfurization with deactivated Raney Ni afforded cholest-5-ene (IXb).<sup>11</sup>

It has thus been shown that although reduction of the 3,5-dieno[3,4-*b*]oxathiane (VIII) with lithium in liquid ammonia resulted in rather non-specific reductive cleavage of the



3,5-dieno[3,4-*b*]oxathiano system at 3,4,5, and 6 positions, it gave the desired 3-eno[3,4-*b*]oxathiane (XI) as a product. Examination of the UV spectrum of the 3-ene[3,4-*b*]oxathiane (XI) thus obtained has then led to a conclusion that, as we have suggested earlier,<sup>4-7</sup> origin of the first absorption bands in the UV spectra of the 3,5-dieno[3,4-*b*]oxathiano (I) and its dithiano (II) systems in the steroid nucleus is from a unique conjugation

14) M. Tomoeda, M. Inuzuka, T. Furuta, M. Shinozuka, and T. Takahashi, *Tetrahedron*, **24**, 959 (1968).

(XVI) of *p*-electrons of oxygen or sulfur and sulfur atoms and  $\pi$ -electrons of 3-C and 4-C atoms in the conformationally rather fixed ring systems I and II. It might be predicted that such systems as I, II, VI, or VII, with the unique delocalized *p*-electron system mentioned above would show an interesting photochemical behavior. The photochemical study with I and VI is underway.

### Experimental<sup>15)</sup>

**Reduction of Chloesta-3,5-dieno[3,4-*b*]oxathiane (VIII) with Lithium in Liquid Ammonia**—To a deep blue solution of 0.63 g of lithium (Li) in a mixture of 75 ml each of liq.  $\text{NH}_3$  and anhyd. ether, a solution of 500 mg of VIII in a mixture of 50 ml of anhyd. ether and 0.26 ml of abs. EtOH was added dropwise in 5 min under cooling with dry ice-abs. EtOH at  $-70^\circ$ . The reaction mixture was stirred for 5 min when abs. EtOH was added dropwise within 3 min to the reaction mixture to destroy the excess Li. After evaporation of most of remaining liq.  $\text{NH}_3$  in 1.5 hr and addition of  $\text{H}_2\text{O}$  to the residue, the product was extracted into ether. The ethereal layer was washed with water and dried (anhyd.  $\text{Na}_2\text{SO}_4$ ). Concentration of the ethereal filtrate gave a brown oil. The reduction was repeated with the same amount of VIII eight times. The total amount of the oily crude product weighed 4.057 g.

This was chromatographed on silica gel (410 g) (Kanto Chemical Co.). Elution with petr. ether (1300 ml) gave a hydrocarbon mixture (IX), mp  $59-62^\circ$  (wt. 245 mg, 6.5%),  $[\alpha]_D^{25} +24^\circ$  ( $c=1.01$ ); IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 1663 (w), 809 (s) ( $-\text{CH}=\text{C}<$ ); UV: an end absorption at  $210 \text{ m}\mu$ ; NMR  $\tau$ : 4.72 (one proton, broad) (vinylic proton), 8.99 (three protons, singlet) (19-H), 9.32 (three protons, singlet) (18-H). The mixture was rechromatographed on silica gel (25 g) when elution with petr. ether (270 ml) afforded a colorless solid, mp  $69-71^\circ$  (wt. 183 mg, 5.1%). Recrystallization from acetone gave cholest-4-ene (IXa) as colorless needles, mp  $71-73^\circ$  (wt. 147 mg, 3.9%). Further recrystallization from the same solvent gave material of mp  $73-75^\circ$ , alone and on admixture with an authentic sample of IXa.<sup>11)</sup> Anal. Calcd. for  $\text{C}_{27}\text{H}_{46}$ : C, 87.46; H, 12.51. Found: C, 87.35; H, 12.63.  $[\alpha]_D^{25} +48^\circ$  ( $c=0.89$ ); IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 1659 (w), 809 (s) ( $-\text{CH}=\text{C}<$ ); UV: transparent above  $220 \text{ m}\mu$ ; NMR  $\tau$ : 4.72 (one proton, broad) (4-H), 8.99 (three protons, singlet) (19-H), 9.33 (three protons, singlet) (18-H). The compound (IXa) gave, on bromination with gaseous bromine, 4 $\beta$ ,5 $\alpha$ -dibromocholestane (XIII), mp  $112-114^\circ$  (30.3%), alone and on admixture with its authentic sample derived from cholest-4-ene.<sup>11)</sup>  $[\alpha]_D^{27} +30^\circ$  ( $c=0.92$ ).

Further elution of the chromatogram with petr. ether (500 ml) afforded a colorless solid, mp  $149-159^\circ$  (wt. 467 mg). This was rechromatographed on silica gel (100 g) when elution with the same solvent (440 ml) gave bis(cholest-4-en-4-yl)disulfide (X) as thin-layer chromatographically homogeneous colorless needles, mp  $174-178^\circ$  (wt. 332 mg, 8.1%). This was recrystallized from ether-acetone, affording material of mp  $190.5-191.5^\circ$  (wt. 198 mg, 4.8%). Further recrystallization from the same solvent gave material of mp  $193-194^\circ$ . Anal. Calcd. for  $\text{C}_{54}\text{H}_{90}\text{S}_2$ : C, 80.72; H, 11.21; S, 9.73. Found: C, 80.72; H, 11.21; S, 7.93.  $[\alpha]_D^{27} +70^\circ$  ( $c=1.03$ ); UV  $\lambda_{\text{max}}^{\text{hexane}}$   $\text{m}\mu$  ( $\epsilon$ ): 224 (19800) ( $>\text{C}=\text{C}-\text{S}-$ ); IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 1610 (w) ( $\text{C}=\text{C}$ ); NMR  $\tau$ : 6.71 (one proton, doublet,  $J=14.5$  cps) (6 $\alpha$ -H), 8.98 (three protons, singlet) (19-H), 9.32 (three protons, singlet) (18-H); Mass spectrum  $m/e$ : 802 ( $(\text{C}_{27}\text{H}_{45}\text{S})_2$ ), 401 ( $\text{C}_{27}\text{H}_{45}\text{S}$ ), 369 ( $\text{C}_{27}\text{H}_{45}$ ).

Further Elution with 4:1 petr. ether-benzene (2700 ml) afforded colorless crystals, mp  $185-190^\circ$  (wt. 699 mg). Recrystallization from ether-acetone gave cholest-3-eno[3,4-*b*]oxathiane (XI) as colorless needles, mp  $189-190^\circ$  (wt. 629 mg, 13.9%). Further recrystallization from the same solvent gave material of mp  $191-192^\circ$ . Anal. Calcd. for  $\text{C}_{29}\text{H}_{48}\text{OS}$ : C, 78.31; H, 10.88; S, 7.48. Found: C, 78.48; H, 10.76; S, 7.68.  $[\alpha]_D^{28} -27^\circ$  ( $c=0.79$ ); UV  $\lambda_{\text{max}}^{\text{hexane}}$   $\text{m}\mu$  ( $\epsilon$ ): 227 (4900) ( $\text{O}-\text{C}_3=\text{C}_4-\text{S}$ ); IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 1648 (s) ( $\text{C}=\text{C}$ ); NMR  $\tau$ : 5.53-6.17 (two protons, multiplet ( $-\text{O}-\text{CH}_2-$ ), 6.99-7.16 (two protons, multiplet) ( $-\text{S}-\text{CH}_2-$ ), 9.14 (three protons, singlet) (19-H), 9.33 (three protons, singlet) (18-H).

Further elution with benzene (4700 ml) afforded 4 $\alpha$ -( $\beta$ -hydroxyethylthio)cholest-5-ene (XII) as colorless needles, mp  $100-105^\circ$  (wt. 1002 mg, 22.0%). Recrystallization from acetone gave material of mp  $108-109^\circ$  (wt. 667 mg, 14.7%). Anal. Calcd. for  $\text{C}_{29}\text{H}_{50}\text{OS}$ : C, 77.96; H, 11.29; S, 7.18. Found: C, 77.89; H, 11.34; S, 7.01.  $[\alpha]_D^{24} -16^\circ$  ( $c=1.10$ ); UV  $\lambda_{\text{max}}$   $\text{m}\mu$  ( $\epsilon$ ): 212 (1700) ( $\text{C}=\text{C}$ ); IR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3256 (s) (OH), 1658 (w) ( $\text{C}=\text{C}$ ); NMR  $\tau$ <sup>16)</sup>: 4.12 (one proton, doublet) (6-H), 6.32 (two protons, triplet,  $J=6$  cps) ( $-\text{O}-\text{CH}_2-$ ), 6.56 (one proton, doublet,  $J=12$  cps) ( $-\text{CH}_2-\text{S}-\text{CH}<$ ), 7.31 (two protons, triplet,  $J=6$  cps) ( $-\text{CH}_2-\text{S}-\text{CH}<$ ), 9.01 (three protons, singlet) (19-H), 9.32 (three protons, singlet) (18-H).

15) Melting points were taken on a Kofler-type hot-plate, and are uncorrected.  $[\alpha]_D$  refers to chloroform, UV absorption spectra to 95% ethanol, and IR spectra to Nujol unless otherwise stated. NMR spectra were run on a Varian Associates A-60 high resolution spectrometer, and the intensities or peak areas were measured by the integrator.

16) The signal due to alcoholic function could not be identified, possibly, owing to its being masked in the strong peak due to the  $-\text{S}-\text{CH}_2-$  group.

**Desulfurization of X with Deactivated Raney Ni: Formation of Cholest-4-ene (IXa)**—A mixture of 125 mg of X and *ca.* 4.8 g of deactivated Raney Ni in 25 ml of AcOEt was refluxed for 5 min. Concentration of the filtrate gave a colorless solid, mp 76—78°, (wt. 106 mg). Recrystallization from acetone gave cholest-4-ene (IXa) as colorless needles, mp 79—81° (wt. 77 mg, 66.9%). Further recrystallization from the same solvent gave material of mp 80.5—81.5°, alone and on admixture with an authentic specimen<sup>17)</sup> derived from cholest-4-en-3-one.  $[\alpha]_D^{25} + 70^\circ$  ( $c=1.07$ ); IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3020 (shoulder), 1662 (w), 809 (s) ( $\text{>C=CH-}$ ).

**Desulfurization of XI with Deactivated Raney Ni: Formation of Cholestan-3-one (XIV)**—A mixture of 242 mg of XI and *ca.* 20 g of deactivated Raney Ni in 50 ml of acetone was refluxed for 5 min. The filtrate was concentrated *in vacuo* to give a colorless oil (204 mg) which was chromatographed over silica gel (20 g) when elution with 1:4 petr. ether–benzene (240 ml) afforded cholestan-3-one (XIV) as colorless needles, mp 125—128° (wt. 93 mg, 44.1%). Recrystallization from MeOH gave material of mp 128—129° (wt. 67 mg, 31.8%), alone and on admixture with its authentic specimen<sup>17)</sup> derived from cholesterol. *Anal.* Calcd. for  $\text{C}_{27}\text{H}_{46}\text{O}$ : C, 83.87; H, 11.99; Found: C, 84.03; H, 11.95.  $[\alpha]_D^{21} + 37^\circ$  ( $c=1.00$ ); IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 1714 (s) (C=O); UV  $\lambda_{\max}$   $\text{m}\mu$  ( $\epsilon$ ): 283 (27) (C=O).

**Desulfurization of XII with Deactivated Raney Ni: Formation of Cholest-5-ene (IXb)**—A mixture of 408 mg of XII and *ca.* 12 g of deactivated Raney Ni in 50 ml of AcOEt was refluxed for 5 min. Concentration of the filtrate gave a solid, mp 58—62°, (wt. 370 mg). This was chromatographed on silica gel (185 g) when elution with petr. ether (900 ml) afforded a solid, mp 62—70° (wt. 135 mg). Recrystallization from acetone gave crude cholest-5-ene (IXb) as colorless needles, mp 83—86°, (wt. 74 mg, 25.0%);  $[\alpha]_D^{22} - 51^\circ$  ( $c=0.91$ ). Further recrystallization from the same solvent gave material of mp 92—93°, alone and on admixture with an authentic sample of IXb<sup>18)</sup> derived from cholesteryl chloride. IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3030 (w) (shoulder), 1673 (w), 831 (s), 799 (s) ( $-\text{CH}=\text{C}$ ).

**Acetylation of XII**—To a solution of 300 mg of XII in 6.0 ml of pyridine, 3.0 ml of acetic anhydride was added and the reaction mixture was kept at room temperature for 3 hr and then poured into ice–water. The deposited solid (mp 74—76°, wt. 316 mg) was filtered off and washed with water and dried *in vacuo*. Recrystallization from EtOH gave the acetate (XV) as colorless needles, mp 79.5—80.5° (wt. 238 mg, 72.6%). Further recrystallization from the same solvent gave material of mp 80—81°. *Anal.* Calcd. for  $\text{C}_{31}\text{H}_{52}\text{O}_2\text{S}$ : C, 76.38; H, 10.72; S, 6.56. Found: C, 76.36; H, 10.78; S, 6.38.  $[\alpha]_D^{25} - 7^\circ$  ( $c=0.89$ ); UV  $\lambda_{\max}$   $\text{m}\mu$  ( $\epsilon$ ): 212 (1500) (C=C); IR  $\nu_{\max}$   $\text{cm}^{-1}$ : 1740 (s), 1251 (s) ( $\text{CH}_3\text{COO}$ ); NMR  $\tau$ : 4.16 (one proton, doublet) (6-H), 5.83 (two protons, triplet,  $J=6$  cps) ( $-\text{O}-\text{CH}_2-$ ), 6.54 (one proton, doublet,  $J=12$  cps) ( $-\text{CH}_2-\text{S}-\text{CH}<$ ), 7.32 (two protons, triplet,  $J=6$  cps) ( $\text{CH}_2-\text{S}-\text{CH}<$ ), 7.96 (three protons, singlet) ( $-\text{CO}-\text{CH}_3$ ), 9.00 (three protons, singlet) (19-H), 9.33 (three protons, singlet) (18-H).

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