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ADDITION TO STEROID POLYENES—III

REACTIVITY OF THE CHOLESTA-5,7,9(11)-TRIENE SYSTEM

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Abstract—The reactivity of the cholesta-5,7-diene system towards 1,4-addition is greatly enhanced by the introduction of a 9(11)-double bond. From the reaction of 3β-acetoxycholesta-5,7,9(11)-triene (I) with maleic anhydride, diethyl diazodicarboxylate and dimethyl acetylene-dicarboxylate three 1,4-adducts were obtained. The vinylene-bridge double bond in these adducts could be selectively removed by catalytic reduction. By a comparative study of the NMR spectra of the adducts and their reduction products it was proved that in each case addition has occurred at the α-side of the steroid molecule and that the maleic anhydride adduct also has the endo-structure.

7-Dehydrocholesteryl acetate has been found to react with diazodicarboxylic esters by addition at C_7, followed by hydrogen abstraction from C_9.[2] Dimethyl acetylenedicarboxylate reacted in a similar way. In this case two products were obtained, resulting from hydrogen abstraction from C_9 and C_{14} respectively.[3] In the ergosterol series it has been observed that introduction of an additional double bond in the 9(11)-position results in a considerable increase in reactivity towards addition to the 5,7-diene system.[4] Whereas ergosteryl acetate has been reported to react with maleic anhydride in boiling xylene with formation of at least five different one-to-one adducts,[5] 9(11)-dehydroergosteryl acetate reacts at appreciably lower temperatures with formation of only one product in good yield.[4] This product is believed to have been formed by 1,4-addition to the 5,7-diene system, resulting in formation of a 5α,8α-bridged compound.[6] Although no additions to the 5,7,9(11)-triene system seem to have been reported in the cholestane series it could be expected that here too an increased reactivity towards 1,4-addition might be observed. 3β-Acetoxycholesta-5,7,9(11)-triene, a compound that had become readily available because of its formation during the pyrolysis of the adduct from 7-dehydrocholesteryl acetate and diethyl diazodicarboxylate[2] was chosen as the triene. Reactions were performed with maleic anhydride, diethyl diazodicarboxylate and dimethyl acetylenedicarboxylate. The results are indicated in Fig. 1.

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[1] Part of the Thesis of A. van der Gen, Amsterdam (1964).

[2] Part I of this series. A. van der Gen, J. Lakeman, M. A. M. P. Gras and H. O. Huisman, *Tetrahedron* **20**, 2521 (1964).

[3] Part II of this series. A. van der Gen, J. Lakeman, U. K. Pandit and H. O. Huisman, *Tetrahedron* **21**, 3641 (1965).

[4] A. Windaus and R. Langer, *Liebig's Ann.* **508**, 105 (1933).

[5] K. Schubert and K. H. Böhme, *Chem. Ber.* **93**, 1878 (1960).

[6] O. Tanaka and E. Mosettig, *J. Amer. Chem. Soc.* **85**, 1131 (1963).

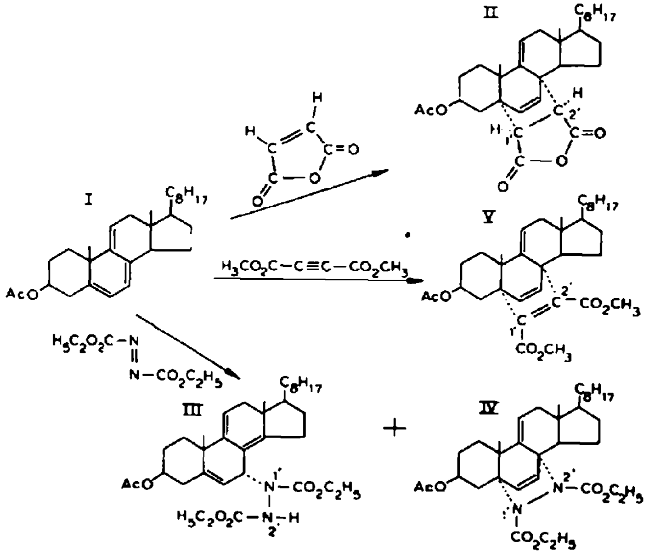

FIG. 1

A. *Maleic anhydride.* With this dienophile a greater reactivity of the 5,7,9(11)-triene system was indeed observed. In the reaction of 7-dehydrocholesteryl acetate with maleic anhydride refluxing in xylene for 8 hr is needed.[7] The triene on the other hand had reacted completely after 4 hr refluxing in benzene with excess maleic anhydride resulting in formation of only one product as indicated by thin-layer chromatography (TLC). After removal of the solvent and the excess dienophile from the reaction mixture a one-to-one adduct was readily obtained in high yield. The IR spectrum displays the absence of all bands whose presence in the starting material was associated with the three conjugated double bonds. (C—H "deformation" at 840 cm^{-1}; C=C "stretch" at 1590 and 1655 cm^{-1}.) The UV spectrum confirms the absence of a conjugated system [$\lambda_{max}^{cyclohex}$: 215 nm ($\varepsilon = 4{,}700$)]. The only reaction mode that leads to a complete disappearance of conjugation is a 1,4-addition. This would give rise to formation of 5α,8α-(1′,2′-endo-dicarboxyanhydrideëthylene)-3β-acetoxy-cholesta-6,9(11)-diene (II).[8] The assignment of structure II is confirmed by the NMR spectrum of the adduct. The C_8- and C_7-vinylic protons on the vinylene-bridge give rise to a pair of doublets centered around δ 6·16.[9] The observed coupling constant is in agreement with the value of 8·2 c/s, expected for two protons with a dihedral angle of 0°.[10] [$J_{8-7} = 8{\cdot}0$ c/s; $\Delta_{8-7} = 22{\cdot}2$ c/s].[11] At δ 5·45 a multiplet absorption from the C_{11}-vinylic proton is observed, partially overlapping the broad 3α-H signal centered at δ 5·02. Centered around δ 3·21 another pair of doublets is found, attributed to the "bridgehead" protons at $C_{1'}$ and $C_{2'}$. Here too the coupling

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[7] Fr. Schenk, K. Bucholz and O. Wiese, *Chem. Ber.* **69**, 2696 (1936) no yield given.

[8] It is assumed at this point that addition takes place from the α-side and that the *endo*-adduct is formed. Subsequent discussion of the NMR spectra of these adducts will show that this is indeed the case.

[9] The intensity of the vinylene-bridge protons in II, IV and V actually measured was 10–15% less than the value expected for two protons.

[10] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959); *J. Amer. Chem. Soc.* **85**, 2870 (1963).

[11] Δ is the difference in chemical shift between the centers of the two doublets.

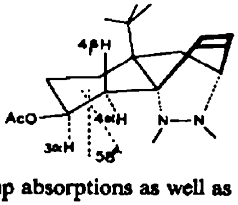
constant agrees with the expected value of 8·2 c/s. [$J_{1'-2'}$ = 8·2 c/s; $\Delta_{1'-2'}$ = 42·1 c/s].[12]

B. *Diethyl diazodicarboxylate.* The reaction with the diazoester had a less specific course than that with maleic anhydride. After 4 hr refluxing in benzene the triene had completely reacted and TLC analysis indicated the presence of two products in about equal quantities. These components were separated by adsorption chromatography over Florisil.

The more polar of the two compounds thus obtained was assigned structure III, that of an adduct formed by nucleophilic addition of the diazoester at C_7, followed by hydrogen abstraction from C_{14} and a shift of the 7(8)-double bond to the 8(14)-position. Structure III, 7α-(1′,2′-dicarbethoxyhydrazo)-3β-acetoxycholesta-5,8(14), 9(11)-triene, is confirmed by its spectral properties. The IR spectrum shows a striking similarity to the spectra of the diazoester-adducts from 7-dehydrocholesteryl acetate, for which the 7α-substituted structure has been proved.[2] For example, a strong signal at 1528 cm^{-1} which is probably due to a combination vibration, is present in all these adducts. Solid-phase spectra display a strong band at 3350 cm^{-1} indicating the presence of a N—H group. A difference between this compound and the earlier obtained addition-abstraction products is of course that in this case the conjugation is only partially lost. [$\lambda_{max}^{cyclohex}$: 213 (ε = 7,900), 228 (ε = 8,400), 236 (ε = 9,700), 243 (ε = 8,900) and 283 nm (ε = 4,200).] The NMR spectrum displays an asymmetrically shaped signal at δ 6·2–7·0 due to the proton attached to the nitrogen. The C_{11}-vinylic proton is found at δ 6·05 and the C_7-β-proton together with the C_6-vinylic proton as a broad multiplet at δ 5·32. The C_{19}-methyl group absorption is found at the same field-strength as in the other addition-abstraction products (δ 1·20) but the C_{18}-methyl group is found at relatively low field (δ 0·82) due to the deshielding effect of the 8(14)-double bond.

The less polar product displays all the spectral features associated with structure IV, 5α,8α-(1′,2′-dicarbethoxyhydrazo)-3β-acetoxycholesta-6,9(11)-diene. In this case no IR bands are found over 3200 cm^{-1} or around 1520 cm^{-1} and the UV spectrum shows no absorption over 220 nm. The NMR spectrum shows the pair of doublets from the vinylene-bridge protons centered at δ 6·36 with J_{6-7} = 8·8 c/s and Δ_{6-7} = 15·6 c/s, the C_{11}-proton at δ 5·35 and the C_3-α-proton at δ 5·18. The ester ethyl groups give rise to a pair of quartets centered at δ 4·05 with $J_{CH_2-CH_3}$ = 7·0 c/s and a pair of triplets centered at δ 1·25 and δ 1·11, both with the same coupling constant.

An additional quartet centered at δ 3·56 could be assigned to the C_4-α-proton by evaluation of its chemical shift, intensity and multiplicity. In general the C_4-α-proton will not be observable as a separate signal because it will absorb at δ-values < 2·0. In the structure at hand however this proton will be greatly deshielded both by the diamagnetic anisotropy of the vinylene-bridge double bond (distance 2·84 Å) and by



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[12] The significance of the methyl group absorptions as well as that of an additional quartet centered at δ 2·92 will be discussed later on.

long-range deshielding by the 5α,8α-bridge atoms. The distance of only 2·64 Å between the 4α-hydrogen atom and the nearest nitrogen atom is expected to result in an appreciable downfield shift.[13] The possibility that this quartet arises from an AB-type spin-spin coupling is excluded by the observations that the absorptions integrate for just one proton and that the pattern is not center-symmetrical but has the double-doublet structure correlated with the low-field part of an AB-spectrum that shows extra splitting due to a weak additional spin-spin coupling. The C_4-β-proton is not observed as a separate signal. The distance between this proton and the nearest nitrogen atom is appreciably larger (3·34 Å) while the distance to the vinylene-bridge is virtually the same (2·74 Å). The strong coupling between geminal protons will result in formation of a doublet by the C_4-α-proton with a coupling constant of 12–15 c/s. This doublet will be split into a quartet by coupling of the C_4-α-H with the C_3-α-H. The dihedral angle of about 58° between these atoms corresponds to a theoretical J-value of ca. 2·5 c/s.[14] The NMR spectrum actually displays one doublet centered at δ 3·67 with $J_{4\alpha-3\alpha} = 4{\cdot}5$ c/s and one doublet at δ 3·44 with the same coupling constant. For $J_{4\alpha-4\beta}$ a value of 13·6 c/s is observed.[15]

C. *Dimethyl acetylenedicarboxylate.* The more vigorous conditions needed in the reaction with this dienophile caused the formation of appreciable amounts of resinous material. Even here though, a crystalline one-to-one adduct could be obtained. The IR spectrum shows many differences compared with those of the addition-abstraction products from the acetylene ester with 7-dehydrocholesteryl acetate,[3] but does not provide conclusive structural evidence. The same is true for the UV spectrum $\lambda_{max}^{cyclohex}$: 215 ($\varepsilon = 13{,}300$) and 256 nm (infl., $\varepsilon = 11{,}200$). The NMR spectrum (Fig. 2) of this adduct however shows, by its great similarity to those of compounds II and IV, that here as well 1,4-addition has taken place, thus giving rise to the formation of 5α,8α-(1′,2′-*cis*-dicarbomethoxyvinylene)-3β-acetoxycholesta-6,9(11)-diene (V). The pair of doublets from the vinylene-bridge protons is now centered at δ 6·27 with $J_{6-7} = 7{\cdot}5$ c/s and $\Delta_{6-7} = 22{\cdot}0$ c/s and the 4α-proton appears as a quartet centered at δ 2·88 with $J_{4\alpha-3\alpha} = 4{\cdot}7$ c/s and $J_{4\alpha-4\beta} = 13{\cdot}8$ c/s. The ester-methyl groups give rise to two singlet-absorptions at δ 3·64 and δ 3·74. In agreement with what is known about the behaviour of other 1,4-adducts from dimethyl acetylenedicarboxylate,[3] adduct V shows a lower thermal stability than the addition-abstraction products and melts with decomposition.

The foregoing results confirm the enhanced reactivity of the cholesta-5,7,9(11)-triene system over the corresponding 5,7-diene system with respect to 1,4-addition at positions 5 and 8. As probable causes for this phenomenon may be mentioned the increased polarizability of the π-electron system in the triene[16] and the decrease in steric hindrance that is associated with the absence of the 9α-hydrogen atom. Observations on Dreiding models indicate that the greatest steric interference towards 1,4-addition from the α-side is exerted by α-axial substituents at positions 4,11,9 and 14. In the 5,7-diene there are two such substituents (the 9α- and 14α-hydrogen atoms) while in the triene this number is reduced to one.

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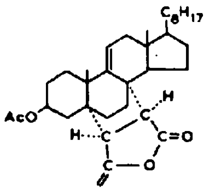
[13] M. Tomoeda, M. Inuzuka and F. Furuta, *Tetrahedron Letters* 1233 (1964).

[14] K. Tori and K. Kitahonoki, *J. Amer. Chem. Soc.* 87, 386 (1965).

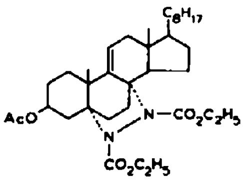
[15] A value of 13·5 c/s was found for $J_{1\alpha-1\beta}$ by J. C. Orr, M. L. Franco, A. D. Cross and F. Sondheimer, *Steroids* 3, 1 (1964) and for $J_{6\alpha-6\beta}$ a value of 14·5 c/s has been reported by M. Tomoeda *et al.*[13]

[16] J. Sauer, H. Wiest and A. Mielert, *Chem. Ber.* 97, 3183 (1964).

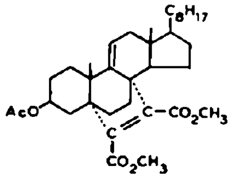
Catalytic reduction of adducts II, IV and V was achieved by treatment with hydrogen and Adam's catalyst at room temperature and atmospheric pressure. The reactions were followed by NMR spectroscopy and stopped after uptake of 1 mole of hydrogen. In this way the 6(7)-double bond in the vinylene bridge could be selectively reduced in each instance. This resulted in formation of compounds VI, VII and VIII. Proof for this highly specific reaction course is obtained from the changes in the NMR spectra that occur as a result of these reductions. This is illustrated in Fig. 2 for the case of the acetylene-ester-adduct. In every instance the pair of doublets at low field, due to the vinylene-bridge protons at C_6 and C_7 disappears during the reduction. The other double bonds are not affected. In agreement with this the NMR spectra of compounds VI, VII and VIII still show absorptions for the C_{11}-vinylic proton and VIII displays a strong IR-band at 1618 cm^{-1} that is assigned to the C═C "stretch" vibration of the ester-activated double bond.



VI



VII



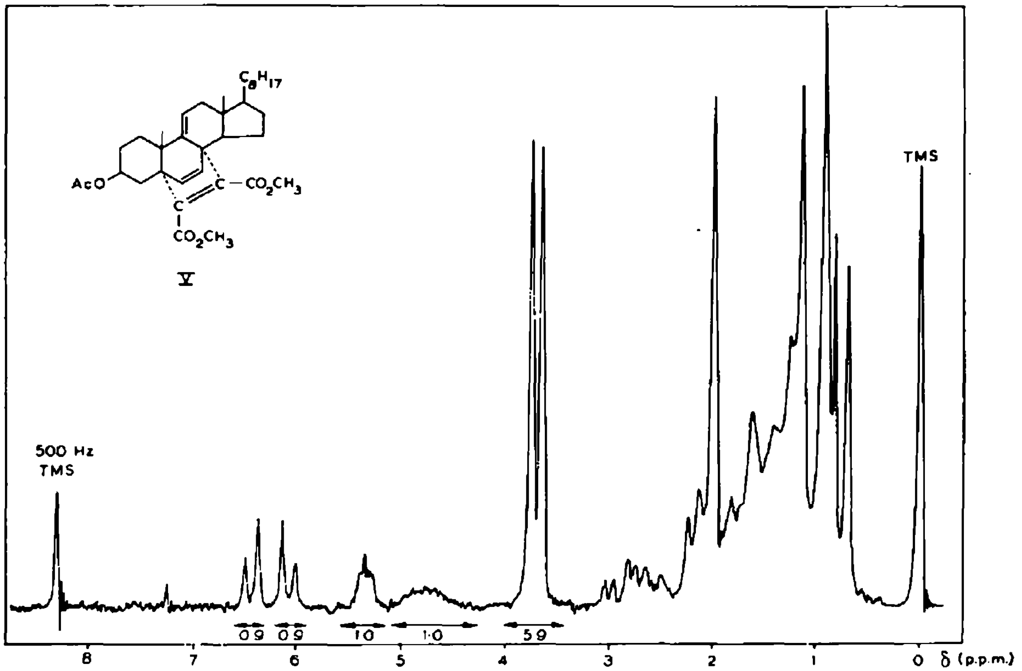
VIII

The course of the reduction thus being established it is possible to evaluate the effect of the introduction of a double bond in the 6(7)-position on the chemical shift of those substituents that show well defined absorptions in the NMR spectra and so draw conclusions about the stereochemistry of the adducts. These shifts are summarized in Table 1.

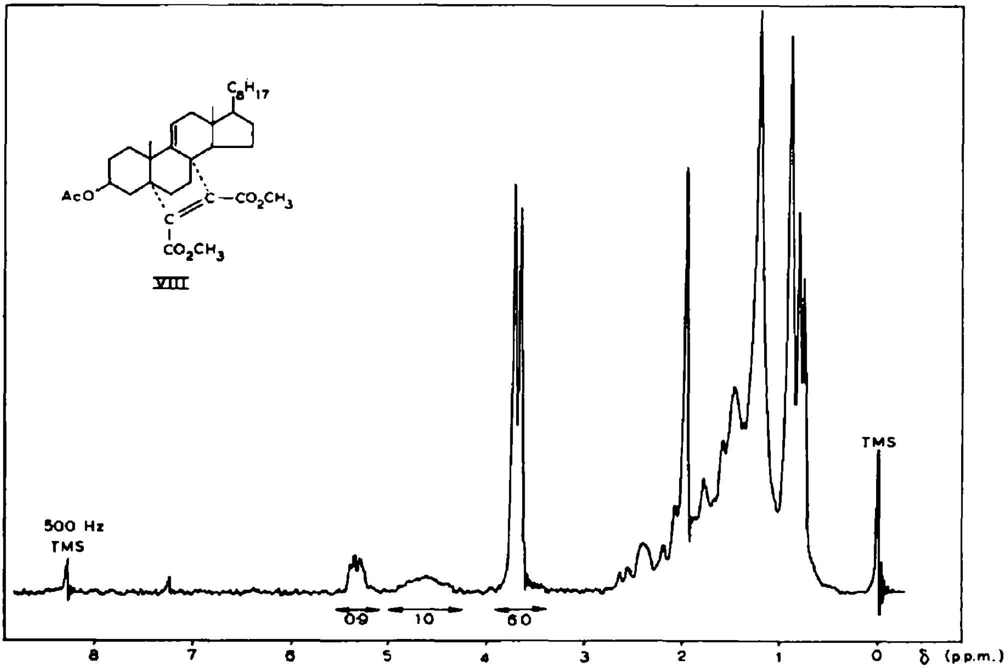
The C_{18}- and C_{19}-axial methyl groups are in each case shielded by the vinylene-bridge double bond. Thus they are situated in the area where this double bond brings about a shift to higher field. As indicated in Fig. 3. using for example the diazoester-adduct, this is only possible if methyl groups and double bond are situated on the same side

TABLE I. NMR SPECTRAL DATA OF THE 1,4-ADDUCTS AND THEIR REDUCTIONS PRODUCTS

Subst.	Before reduction			After reduction			Δδ ppm × 10^2		
	MA	N═N	C≡C	MA	N═N	C≡C	MA	N═N	C≡C
C_6H-C_7H	6·16	6·36	6·27	absent	absent	absent	—	—	—
	pair of doublets								
C_{18}-CH_3	0·64	0·70	0·70	0·73	0·76	0·77	9	6	7
C_{19}-CH_3	1·11	1·16	1·13	1·25	1·24	1·22	14	8	9
C_{11}-H	5·45	5·38	5·36	5·53	5·50	5·45	8	12	9
Side-	0·85	0·85	0·83	0·83	0·83	0·81	−2	−2	−2
chain	0·94	0·93	0·91	0·92	0·91	0·90	−2	−2	−1
Acetate-CH_3	2·08	2·03	1·99	2·02	1·99	1·96	−6	−4	−3
C_3-α-H	5·14	5·18	4·77	4·98	5·04	4·63	−16	−14	−14
C_4-α-H	ca.2·92	3·56	2·87	not	3·27	2·51	—	−29	−36
	quartets			visible	quartets				
$C_{1'}H$-$C_{2'}H$	3·21			3·10			−11		
	pair of doublets			pair of doublets					



acetylene ester adduct (V)



reduced acetylene ester adduct (VIII)

Fig. 2

of the molecule. The β-position of the C_{18}- and C_{19}-methyl groups being well established this proves that the vinylene bridge is on the β-side of the molecule which means that adducts II, IV and V have been formed by addition of the appropriate dienophiles at the α-side of the steroid-molecule.

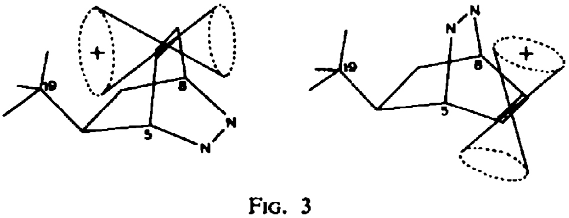


FIG. 3

The C_{11}-vinylic proton also lies in the "shielding cone" of the bridge double bond and by consequence is shifted downfield on reduction. For those substituents that are situated in or near the plane of the double bond reduction is accompanied by an upfield shift which is strongly dependent on the distance. The acetate-methyl signal is shifted to a small extent only but the C_3-α-proton absorption is shifted considerably while the greatest effect is displayed by the C_4-α-proton quartets. As expected, the positions of the side-chain-methyl signals do not undergo significant changes.

A special case is exhibited by the $C_{1'}$ and $C_{2'}$ bridgehead-protons. As indicated in Fig. 4, these protons will be subjected to shielding effects of opposite sign, depending on an *exo-* or *endo*-configuration of the adduct.[17] The $C_{1'}$ and $C_{2'}$ protons in adduct II are deshielded by the vinylene-bridge double bond as is shown by the fact that the pair of doublets caused by these protons distinctly moves to higher field on reduction

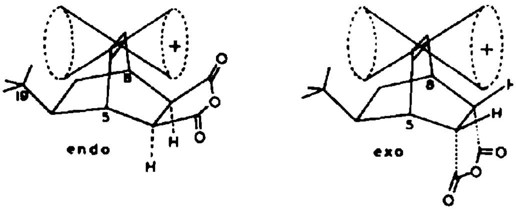


FIG. 4

of the double bond. This proves that the adduct of maleic anhydride and 3β-acetoxycholesta-5,7,9(11)-triene in addition to having the 5α,8α-bridged structure, also has the *endo*-configuration.

EXPERIMENTAL

5α,8α-(1′,2′-Dicarboxyanhydrideëthylene)-3β-acetoxycholesta-6,9(11)-*diene* (II). 3β-Acetoxycholesta-5,7,9(11)-triene (1000 mg; 2·4 mmoles) was dissolved in 11 ml benzene together with maleic anhydride (1500 mg; 15 mmoles) (freshly crystallized from $CHCl_3$) and refluxed for 4 hrs in a N_2 atm. The solvent and the excess dienophile were then removed at red. press. at temp not exceeding 100°. The remaining solid was crystallized from acetic acid–water. According to the IR spectrum the product thus obtained still contained some maleic anhydride, which was subsequently removed by crystallization from MeOH. This yielded II (950 mg; 77%) as colourless needles with m.p. 181–182°, α_D^{20} + 88°. $\lambda_{max}^{cyclohex}$: 214 nm ($\varepsilon = 4{,}700$). ν_{max} at 1860, 1775, 1730, 1095, 1075, 1025, 950, 925 and

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[17] R. R. Fraser, *Canad. J. Chem.* **40**, 78 (1962).

905 cm⁻¹. (Found: C, 75·95; H, 8·75; O, 15·51; $C_{33}H_{46}O_5$ requires: C, 75·82; H, 8·87; O, 15·31%).[18]

5α,8α-(1′,2′-Dicarbethoxyhydrazo)-3β-acetoxycholesta-6,9(11)-*diene* [IV] *and 7α-(1′,2′-dicarbethoxyhydrazo)-3β-acetoxycholesta*-5,8(14),9(11)-*triene* (III). 3β-Acetoxycholesta-5,7,9(11)-triene (2·0 g; 4·8 mmoles) was dissolved in 20 ml benzene, diethyl diazodicarboxylate (3·0 g; 17 mmoles) was added and the mixture was refluxed for 4 hrs in a N_2 atm. After removal of the solvent and the excess diazoester at red. press. on a steambath, the remaining oil was dissolved in 10 ml benzene and chromatographed over 150 g of Florisil.[19] Eluted by 200 ml benzene with 5% ethyl acetate was 610 mg, 22%, 1,4-adduct IV as a colourless oil, showing a single spot in TLC. No UV absorption over 215 nm, ν_{max} at 1730, 1690, 1280, 1250, 1080, 1025, 950, 915 and 815 cm⁻¹. Eluted by 250 ml benzene with 10% ethyl acetate was 590 mg, 21%, of a mixture of about equal quantities of III and IV. Eluted by another 200 ml benzene with 10% ethyl acetate was 550 mg, 20%, addition-abstraction product III as a pale yellow oil that solidified on standing and showed a single spot in TLC. $\lambda_{max}^{cyclohex}$: 213 (ε = 7,900), 228 (ε = 8,400), 236 (ε = 9,700), 243 (ε = 8,900) and 283 nm (ε = 4,200). ν_{max} at 3350, 1730, 1705, 1250, 1065, 1030 and 765 cm⁻¹. The NMR spectrum displays signals at: δ 6·2–7·0 (m,1p,N-H), δ 6·05 (m,1p,11-H), δ 5·32 (m,2p,6-H + 7β-H), δ 2·00 (s,acetate-CH_3), δ 1·20 (s,19-CH_3) and δ 0·82 (s,18-CH_3). The estermethyl groups give rise to a quartet, centered at δ 4·13 with $J_{CH_2-CH_3}$ = 6·1 c/s and a triplet at δ 1·26 with the same coupling constant. Identification of the chromatographic fractions was achieved most conveniently with TLC. The R_f-ratio of compounds IV and III varies strongly with the system used. Good separation with R_f-values of 0·73 and 0·58 was realized by using silicagel–diisopropyl-ether (det. $SbCl_3$ in nitrobenzene).

*5α,8α-(1′,2′-*cis*-Dicarbomethoxyvinylene)-3β-acetoxycholesta*-6,9(11)-*diene* (V). 3β-Acetoxycholesta-5,7,9(11)-triene (600 mg; 1·4 mmoles) was dissolved in 25 ml *p*-xylene. Dimethyl acetylenedicarboxylate (100 mg; 7 mmoles) was added and the mixture refluxed for 17 hr in a N_2 atm. The dark, viscous oil that remained after evaporation of the solvent and the excess dienophile at red. press. on a steambath was dissolved in 15 ml warm methyl cyanide. On standing at 0° the 1,4-adduct V crystallized in colourless needles yield 280 mg (35%), m.p. 192–194° (dec. 1). $\lambda_{max}^{cyclohex}$; 215 (ε = 13,300) and 256 nm (infl. ε = 11,200). ν_{max} at 1740, 1725, 1620, 1590, 1275, 1245, 1120, 1025 and 825 cm⁻¹. (Found: C, 74·26; H, 9·05; O, 16·98; $C_{35}H_{50}O_6$ requires: C, 74·17; H, 8·89; O, 16·94%).

Catalytic reduction of the 1,4-*adducts*

5α,8α-(1′,2′-Dicarboxyanhydrideëthylene)-3β-acetoxycholest-9(11)-*ene* (VI). Adduct II (500 mg; 0·96 mmole) was added to a previously hydrogenated suspension of 50 mg Adam's catalyst in 30 ml ethyl acetate and hydrogenated at room temp and atm. press. As indicated by NMR spectroscopy, reduction of the 6,7-double bond had occurred for 85% after 24 hr and was complete after 3 days. The H_2 uptake at that time was 25 ml (1·15 moles). In this way a quantitative yield of the 6,7-dihydro compound VI with m.p. 193–195° was obtained. The product displayed no UV absorption over 215 nm and had ν_{max} at 2975, 1860, 1770, 1725, 1255, 1030, 940, 930 and 910 cm⁻¹. (Found: C, 75·36; H, 9·16; O, 15·10; $C_{33}H_{48}O_5$ requires: C, 75·53; H, 9·22; O, 15·25%).

5α,8α-(1′,2′-Dicarbethoxyhydrazo)-3β-acetoxycholest-9(11)-*ene* (VII). Hydrogenation of IV in a way similar to that described for adduct II resulted in uptake of 1 mole of H_2 in 2·5 hr. The reaction product VII was obtained as an oil that showed a single spot in TLC. $\lambda_{max}^{cyclohex}$: 211 (ε = 4,300) and 250 nm (infl. ε = 1,300). ν_{max} at 2990, 1720, 1695, 1305, 1260 and 1095 cm⁻¹.

*5α,8α-(1′,2′-*cis*-Dicarbomethoxyvinylene)-3β-acetoxycholest*-9(11)-*ene* (VIII). Adduct V (300 mg; 0·7 mmole) was reduced in a manner, analogous to that outlined for the other 1,4-adducts. Uptake of 1 mole of H_2 was completed in 35 min. On crystallization from MeOH–water the 6,7-dihydro

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[18] Complete oxidation of the 1,4-adducts in C and H analyses was achieved by covering the sample with WO_3.

[19] Separation is appreciably hampered by the presence of free diazoester because this compound decomposes rapidly when brought in contact with absorbentia such as Alumina and Florisil with formation of N_2, CO_2 and the corresponding hydrazo ester. This dilemma is overcome by stirring a soln. of the crude reaction mixture in an inert solvent for 30 min at 50° in the presence of such an absorbent. The 1,2-dicarbethoxyhydrazine is absorbed more strongly than the other reaction products and does not interfere with the subsequent separation.

compound VIII was obtained as needles with m.p. 177–178·5° $\lambda_{\max}^{\text{EtOH}}$: 215 ($\varepsilon = 6{,}000$) and 244 nm (infl. $\varepsilon = 2{,}800$). $\nu_{\max}$ at 2970, 1720, 1620, 1250 and 1030 cm^{-1}. (Found: C, 74·05; H, 9·41; O, 16·69; $C_{35}H_{52}O_6$ requires: C, 73·91; H, 9·22; O, 16·88%).

M. ps are uncorrected. UV, IR and NMR measurements were conducted as described in Part II.

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