85. Acid-Catalysed Backbone Rearrangement of Cholesta-6,8(14)-dienes

by **Rong-Ming Liu**[a]), **Xavier F. D. Chillier**[a]), **Philippe Kamalaprija**[b]), **Ulrich Burger**[b]), and **Fazil O. Gülaçar**[a])*

[a]) Laboratoire de Spectrométrie de Masse, Sciences I, 16 boulevard d'Yvoy, CH–1211 Genève 4
[b]) Département de Chimie Organique, Université de Genève, CH–1211 Genève 4

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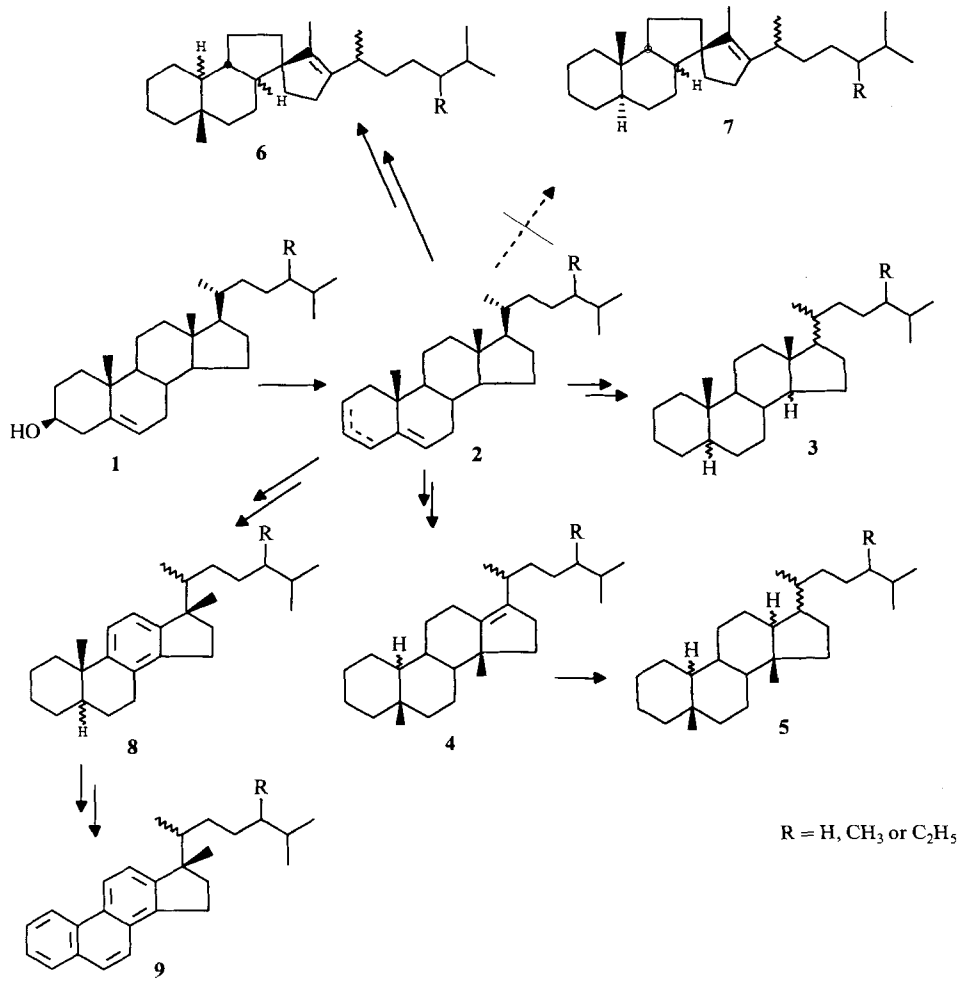
Rearrangement of 5α- and 5β-cholesta-6,8(14)-dienes (**13a** and **13b**, resp.) in the presence of anhydrous toluene-4-sulfonic acid in acetic acid leads to 5α- and 5β-12(13→14)-*abeo*-cholesta-8,13(17)-dienes (**15a** and **15b**, resp.) *via* 5α- and 5β-cholesta-8,14-dienes (**14a** and **14b**, resp.), respectively. Epimerization at C(20) of the spirosteradienes **15a** and **15b** occurs with increasing reaction time. Molecular-mechanics calculation of the relative stabilities of these compounds and of congeners thereof is in agreement with the observed reaction pathway.

Introduction. – Steroidal molecular fossils encountered in sediments, crude oils, and coals are the diagenetic products of stenols and stanols occurring widely in living organisms. Steroids released from the source organisms after their death are incorporated into the surface sediments, then progressively buried. During the burying process, which may last up to several hundreds of million years, the original compounds undergo diagenesis, *i.e.*, a variety of geochemical transformations leading to a multitude of compounds. If these latter preserve enough structural characteristics so that their biological precursors can be inferred, they are called 'biological markers' or 'molecular fossils' [1].

The diagenesis of steroidal precursors in recent and ancient sediments have been the subject of many field studies. Profile analyses of contemporary and ancient sediments for steroidal biomarkers allowed the study of the influence of the environmental conditions at the time of deposition (salinity and oxicity of the water column and of the water-sediment interface, bacterial activity, mineral composition of the sediment) and the establishment of some of the sequences of the reactions occurring in the geosphere (see *e.g.* [2]). We now know that the first stage of the major pathway in the diagenesis of sterols is dehydration leading to the corresponding Δ^2- and Δ^3-steroids. Depending on the composition of the sediment and its thermal history, these olefins undergo various reactions such as direct hydrogenation to steranes, dehydrogenation to more unsaturated and ultimately monoaromatic and triaromatic steroid hydrocarbons. In ancient sediments having been subjected to higher temperature, partial degradation of the side chain is also observed. Another phenomenon which is commonly noticed is isomerization at the chiral centres and/or backbone rearrangements. The major pathways of the diagenesis of the Δ^5-sterols **1** in the geosphere are shown in *Scheme 1*. Although most of these reactions have been inferred from field analyses, laboratory simulation has been useful for identifying the reaction intermediates and understanding the reaction mechanisms. *E.g.*, the rearrangement of cholest-5-ene in the presence of toluene-4-sulfonic acid (TsOH) in acetic acid (AcOH) [3] [4] leads to the backbone-rearranged steroids of structure **4** (R = H) and **6** (R = H), commonly called 'diasterenes' and 'spirosterenes'; the latter are biological

Scheme 1. *Principal Transformation Pathways of Δ^5-Sterols in Sediments*



markers which are common in clay sediments but generally absent in carbonate sediments. It can, therefore, be concluded that their formation in the geosphere is due to the catalytic effects of the acid sites on the surfaces of clay minerals [5]. Laboratory acid-catalysed rearrangements of Δ^7-steroids have also been studied [5] [6] and shown to lead to spirosterenes of structure **7**, which are found in some sediments [7]. These spirosterenes may, therefore, be considered as specific biomarkers for the input of Δ^7-sterols.

We present here the results of studies of the rearrangements of two steradienes, namely 5α- and 5β-cholesta-6,8(14)-dienes (**13a** and **13b**, resp.), in the presence of TsOH in AcOH. These dienes were obtained from the dehydroxylation of cholesta-5,7-dien-3β-ol (**10a**). We postulate that they are the first intermediates of the sedimentary diagenesis of sterols containing two C=C bonds in the B ring (7,8-didehydrosterols).

Since the intermediates and products of their rearrangement were all identified by spectroscopic techniques, reaction mechanisms can be proposed. The relative thermodynamic stabilities of these compounds and other steradiene isomers were computed by molecular-mechanics calculations. These data yielded information on the preferred geometries of the compounds and showed that the reaction pathways paralleled the thermodynamic stabilities of the molecules involved.

Results. – *Dehydroxylation of 7,8-Didehydrocholesterol* (**10a**). The dehydroxylation of **10a** was attempted by tosylation followed by $LiAlH_4$ reduction. The mass spectrum of the main product shows a molecular ion at m/z 368 corresponding to a doubly unsaturated compound. However, ^{1}H-NMR spectroscopy reveals the presence of a cyclopropyl unit (signals at 0.06 and 0.42 ppm) and shows a single olefinic proton (5.15 ppm). The compound was shown by ^{13}C-NMR, DEPT-135, ^{1}H,^{1}H-COSY and HMQC-spectroscopy [8] to be 3,5-cyclocholest-7-ene (**11**). No other steradiene was present in significant amount in the reaction mixture (*Scheme 2*). Characteristic ^{1}H- and ^{13}C-NMR data of **11** are listed in *Table 1*.

NaI/Zn Reduction of cholesteryl tosylate is reported to lead to cholest-5-ene without formation of a 3,5-cyclo derivative [9]. Applied to tosylate **10b**, this method led to a mixture containing mainly three compounds **12**, **13a** and **13b** in a ratio of 7:1:3. Normal-phase HPLC separation of the mixture yielded two fractions. The GC/MS of the second fraction reveals the presence of an almost pure component with the molecular ion at m/z 366 corresponding to three unsaturations. ^{1}H-NMR Spectroscopy shows only two olefinic proton signals, whereas the ^{13}C-NMR spectrum exhibits four sp^2 C-atoms (see *Table 1*). A cyclopropylic H-resonance at 0.48 ppm and comparison of the spectra with those of **11** and **13a** are consistent with the structure of 3,5-cyclocholesta-6,8(14)-diene (**12**) for this component (*Scheme 2*).

The GC/MS of the first HPLC fraction indicates the presence of two components with $M^{+\cdot}$ at m/z 368. Identical fragmentation characteristics suggest that they are configura-

Scheme 2

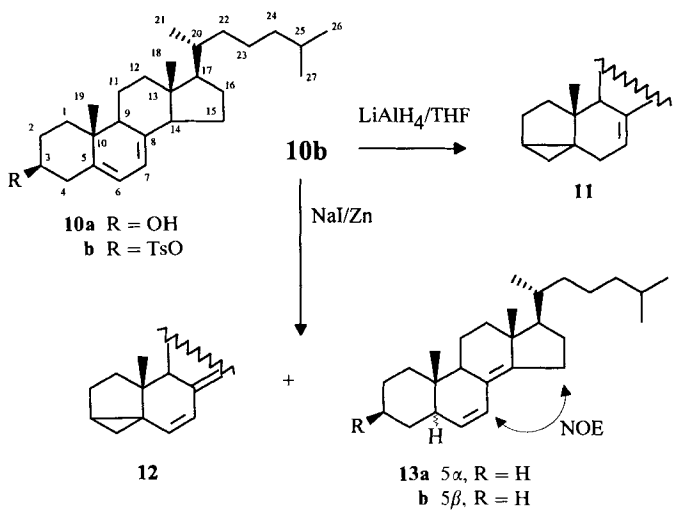


Table 1. *Selected ^{13}C- and ^{1}H-NMR Chemical Shifts* [ppm], *Multiplicities and Apparent Scalar Coupling Constants* J [Hz] *of Compounds* **11–13**, **14b** *and* **15b** *in* $CDCl_3$ (9.4 T)

	11		**12**		**13a**	
	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$
C(3)	25.1	1.12 (*m*)	26.5	1.3 (*m*)		
C(4)	11.4	0.06, 0.42	15.6	0.48, 0.81		
C(5)	41.4	–		–	47.1	2.0 (*m*)
C(6)	29.4	2.52, 1.5	130.6	5.2 (*d*, *J* = 9.8)	130.9	5.27 (*dd*, *J* = 10, 1.8)
C(7)	117.1	5.15 (*dd*, *J* = 5.5, 2.2)	124.1	6.16 (*d*, *J* = 9.8)	125.1	6.1 (*dd*, *J* = 10, 3)
C(8)	139.9	–	124.6	–	125.6	–
C(14)	55.4	1.90	147.1	–	146.8	–
C(15)	25.4	1.52, 1.79	25.2	2.4 (*m*)	24.9	2.35 (*m*)
C(18)	18.4	0.93	19.0	0.93	19.3	0.9
C(19)	12.0	0.58	17.0	0.79	11.2	0.61

	13b		**14b**		**15b**	
	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{1}H)$
C(3)						
C(4)						
C(5)	45.6	1.69 (*m*)			40.9	1.37
C(6)	130.4	5.54 (*dd*, *J* = 10, 5.2)				
C(7)	123.8	6.04 (*d*, *J* = 10)				
C(8)	125.3	–		–	–	
C(14)	146.4	–		–	66.9 (spiro)	–
C(15)	24.9	2.4 (*m*)	116.9	5.37		
C(18)	19.0	0.89	18.92	1.1	9.9	1.38 (*t*, *J* = 1.8)
C(19)	23.50	0.72	23.0	0.84	28.6	1.03

tional isomers. They could be separated and isolated by reversed-phase HPLC. The GC elution order of the two components is the same as on reversed-phase HPLC. The UV absorption spectra of both compounds indicate a conjugated diene system extending over two rings (λ_{max} 248.9 and 252.3 nm, resp., in order of elution). Detailed NMR studies of these compounds allowed their identification as 5β- and 5α-cholesta-6,8(14)-diene (**13b** and **13a**, resp.; *Scheme 2*, *Table 1*).

^{1}H-NMR Spectra of both **13a** and **13b** show two olefinic protons. The possibility of a $\Delta^{6,8(9)}$ skeleton is excluded on the basis of H,H-COSY.DQF and NOESY correlations and of the UV absorptions. The NOESY spectrum of **13a** shows a dipolar interaction between H–C(7) and an allylic proton at 2.35 ppm. This allylic proton has a geminal partner at 2.25 ppm. The HSQC spectra prove that the two allylic protons are bound to the same C-atom (24.90 ppm). The skeleton of cholesta-6,8-diene cannot account for a dipolar coupling between H–C(7) and an allylic CH_2 group. Analogous observations were made for **13b**. The fine structures of the olefinic protons, *i.e.*, the coupling of H–C(5) with H–C(6) and H–C(7) allow to assign the configuration at C(5). In the case of **13a**, a vinylic (1.6 Hz) and an allylic coupling (3.2 Hz) are observed, corresponding to a dihedral angle close to 90° between the H–C(5) and H–C(6) bonds. In the case of **13b**, on the other hand, a relatively large vinylic (5.7 Hz) and no detectable allylic coupling is observed. This agrees well with a H–C(5)/H–C(6) dihedral angle close to 40°. Energy minimization of the two structures **13a** and **13b** by molecular-mechanics calculations (MM+) leads to 91° and 38°, respectively, for this angle.

Acid-Catalysed Rearrangement of 5α- and 5β-Cholesta-6,8(14)-dienes (**13a** and **13b**, resp.). The product distribution of the rearrangement of **13a** and **13b** in the presence of

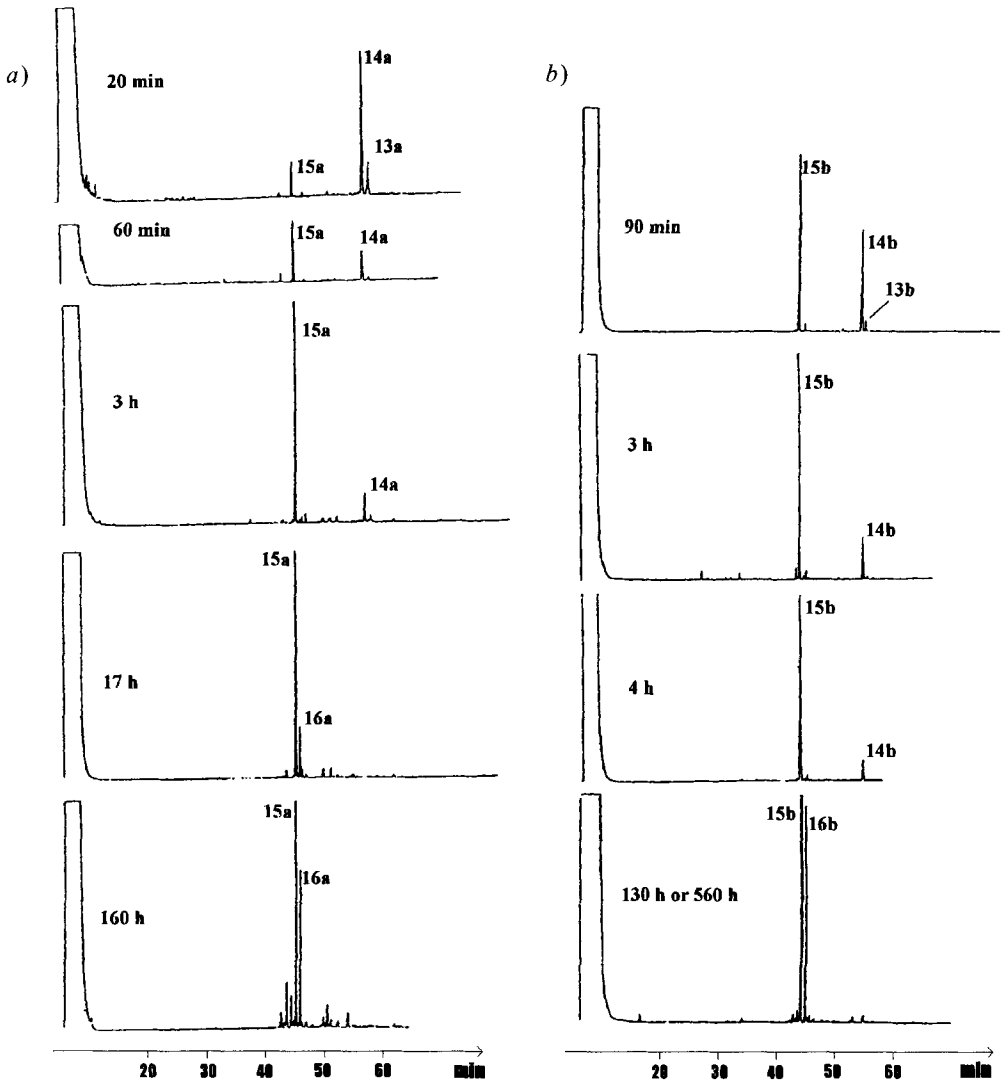
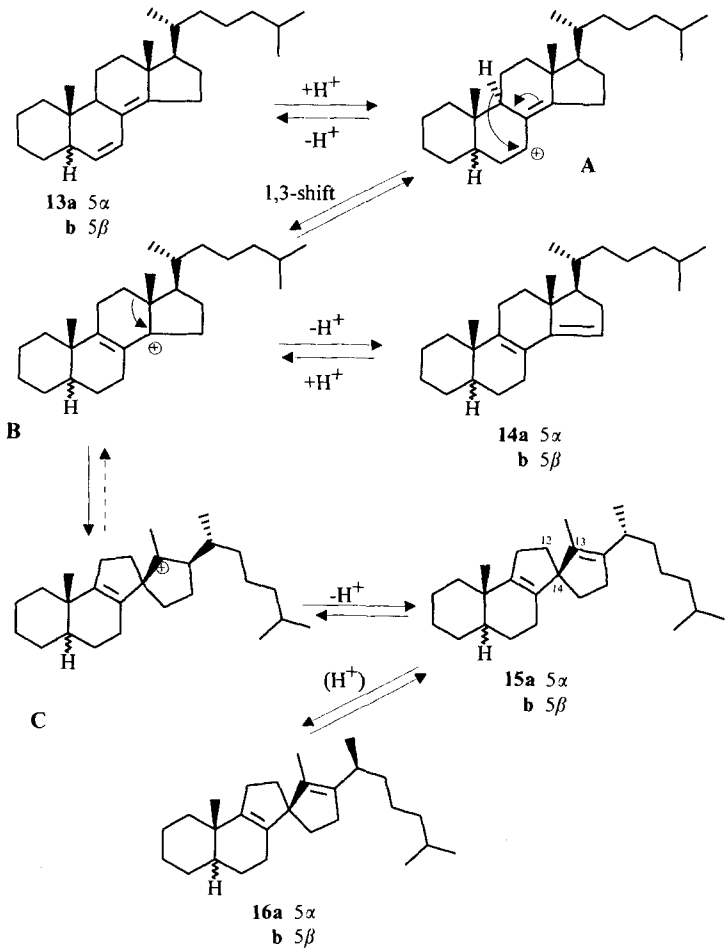


Figure. *Gas chromatograms showing the evolution of the product distribution on acid treatment* (TsOH/AcOH) *of* a) *5α-cholesta-6,8(14)-diene* (**13a**) *and* b) *5β-cholesta-6,8(14)-diene* (**13b**). See *Scheme 3* for structures.

TsOH in AcOH at 70° evolved with reaction time as shown by GC monitoring (*Fig.*). The two starting compounds behaved in a similar way. Their content in the mixture decreased rapidly, and they had disappeared almost completely after 1 h. Meanwhile, intermediate products **14a** and **14b** appeared, which, after 3 h, were almost completely replaced by **15a** and **15b**, respectively. With increasing reaction time, the new components **16a** and **16b** with slightly longer retention times showed up, at the expense of **15a** and **15b**, respectively. After approximately one week, the relative amounts of **15a** *vs.* **16a** and **15b** *vs.* **16b**

Scheme 3



were almost the same and did not change further with time. GC/MS Analyses show that all these compounds are isomers of the starting steradienes. The mass spectra of **14a** and **14b** are very similar, as are those of **15a** and **15b** on the one hand and those of **16a** and **16b** on the other. Finally, the mass spectra of **15a** and **16a** are virtually identical, as are those of **15b** and **16b**. These data suggest that the configuration of the A/B ring junction of the starting dienes **13a** and **13b** is preserved in the **a** and **b** series, and that the pairs **15a**/**16a** and **15b**/**16b**, respectively, are epimers.

Compounds **15a**/**b** and **16a**/**b** all have their UV absorption maxima below 200 nm; the two C=C bonds are, therefore, not conjugated. Component **15b** could be isolated and fully characterized. The spectroscopic data (see *Table 1*) indicate unambiguously that component **15b** is 12(13→14)-*abeo*-5β-cholesta-8,13(17)-diene. Since the only acyclic chiral centre likely to epimerize is at C(20), component **16b** is, therefore, the (20*S*)-epimer of **15b**. Note that the slow acid-catalysed isomerization at C(20) of $\Delta^{13(17)}$-steroids is well documented [3] [10] [11].

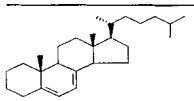
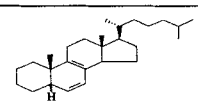
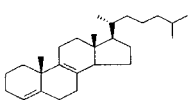
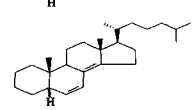
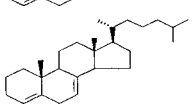
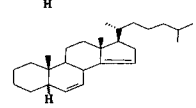
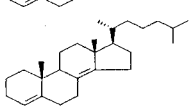
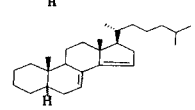
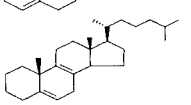
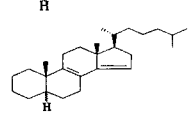
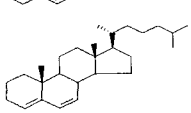
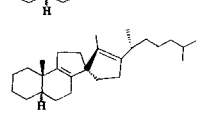
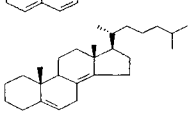
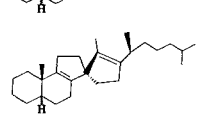
The ^{1}H-NMR spectrum of **15b** shows no olefinic proton, while ^{13}C-NMR reveals four signals between 135–145 ppm, one of them being significantly weaker than the others. DEPT-135 and DEPT-90 spectra allow the detection of 3 CH, 5 Me, and 13 CH_2 groups. From the H,C-COSY spectrum it is seen that one of the *C*H atoms (at 32.5 ppm) is bound to an allylic proton at 2.46 ppm. H,H-COSY.DQF shows that this allylic proton couples with a Me *d* at 0.95 ppm and a CH_2 *m* centred at 1.25 ppm. Moreover, the NOESY spectrum reveals that the allylic proton is close to a Me group (δ(^{13}C) 9.9 ppm and δ(^{1}H) 1.38 ppm) bound to a C=C moiety. Finally, the presence of a spiro C-atom is suggested by the resonance of a tetrasubstituted C-atom at 66.86 ppm [12].

We could isolate only a small quantity of **14b** in sufficient purity for NMR studies. Its UV absorption (λ_{max} 250 nm) indicates a conjugated diene system extending over two rings. The NMR data (see *Table 1*) of **14b** is consistent with the structure of 5β-cholesta-8,14-diene; hence **14a** is its 5α-epimer.

Only one olefinic proton appears in the ^{1}H-NMR spectrum of **14b**, and the allylic proton region (1.9–2.5 ppm) integrates for 6 H-atoms. ^{13}C-NMR shows only 3 olefinic C-atoms, and ^{13}C-DEPT reveals that only one of them is linked to a H-atom. Except the lacking of a signal for the fourth olefinic C-atom, the data are in agreement with a $\Delta^{8,14}$-steroid system. Comparison with the published spectra of 3β-hydroxy-5β-cholesta-8,14-diene [13] shows a perfect concordance for the ^{13}C-NMR chemical shifts of atoms C(9) to C(18) and C(20) to C(27).

Discussion. – The reductive removal of a tosyloxy group with NaI/Zn in glyme has been reported to occur without formation of 3,5-cyclo-steroids in the case of several 3β-(tosyloxy)-Δ^5-steroids [9]. Moreover, no migration of the 5-double bond has been

Table 2. *Calculated Relative Stabilities of Cholestadiene and Spirocholestadiene Isomers*

	Structural features	*E* [kcal/mol]		Structural features	*E* [kcal/mol]
	$\Delta^{5,7}$	48.37		$\Delta^{6,8}$, 5β, (20*R*)	45.04
				$\Delta^{6,8}$, 5α, (20*R*)	46.68
	$\Delta^{4,8}$, (20*R*)	47.19		$\Delta^{6,8(14)}$, 5β, (20*R*)	42.36
				$\Delta^{6,8(14)}$, 5α, (20*R*)	43.17
	$\Delta^{4,7}$, (20*R*)	46.39		$\Delta^{6,14}$, 5β, (20*R*)	42.47
				$\Delta^{6,14}$, 5α, (20*R*)	42.35
	$\Delta^{4,8(14)}$, (20*R*)	47.77		$\Delta^{7,14}$, 5β, (20*R*)	43.10
				$\Delta^{7,14}$, 5α, (20*R*)	41.76
	$\Delta^{5,8}$, (20*R*)	44.52		$\Delta^{8,14}$, 5β, (20*R*)	40.20
				$\Delta^{8,14}$, 5α, (20*R*)	40.38
	$\Delta^{4,6}$, (20*R*)	44.04		spiro, $\Delta^{8,13(17)}$, 5β, (20*R*)	38.47
				spiro, $\Delta^{8,13(17)}$, 5α, (20*R*)	38.97
	$\Delta^{5,8(14)}$, (20*R*)	44.77		spiro, $\Delta^{8,13(17)}$, 5β, (20*S*)	38.56
				spiro, $\Delta^{8,13(17)}$, 5α, (20*S*)	39.06

observed during the process. However, treatment of **10** with NaI/Zn yields **12** as the main product, and the compounds **13a** and **13b** resulting from the reductive removal have the C=C bonds migrated from the 5,7- to the 6,8(14)-positions. Molecular-mechanics calculations suggest that the driving force might be the thermodynamic stabilities of the compounds. The total energies (E) of a set of steradienes calculated for the geometries of global-energy minimum are listed in *Table 2*. The energy minimizations and total-energy calculations were carried out with the HYPERCHEM™ program package using MM+ empirical force field. Note that the absolute values of energy from these calculations are not meaningful, but the relative energies compare well with the heats of formation. The results show that, amongst the cholestadienes which may be produced from the original $\Delta^{5,7}$-steroid by single-step 1,2-H migration, 5β- and 5α-cholesta-6,8(14)dienes are the most stable isomers.

From the evolution of the product distribution, the pathway of the rearrangements of 5α- and 5β-cholesta-6,8(14)-dienes (**13a** and **13b**) in the presence of TsOH/AcOH may be as suggested in *Scheme 3*. Cholesta-8,14-dienes (**14a**/**14b**) are produced by the well-known reversible carbocation-alkene interconversions [10]. It has been observed that the C=C bond isomerization in monounsaturated steroidal olefins in the presence of TsOH/AcOH at 85° proceeds only *via* the intermediate tertiary carbocations [14] [15]; *e.g.* 1-, 2-, 3- and 6-unsaturated cholestenes do not isomerize while the pair of the 4- and 5-unsaturated cholestenes equilibrates. In the case of cholesta-6,8(14)-dienes, however, the allylic carbocation **A** is obviously the intermediate for the migration of the 6-double bond. Again, among the steradienes which may be produced from the isomerization of **13a** and **13b** by the intermediates of tertiary and/or allylic carbocations, cholesta-8,14-dienes **14a** and **14b** are the thermodynamically most stable ones (see *Table 2*).

The formation of spiro compounds **15a**/**15b** from carbocation **B** by ring contraction (→ **C**) releases the steric energy associated with the C/D ring system of **14a**/**14b**. Although this contraction is probably reversible, as with monounsaturated Δ^{14}-steroid [5], prolonged reaction leads to the thermodynamically most stable $\Delta^{8,13(17)}$-spirosteroids **15a**/**15b** (see *Table 2*). Finally, the isomerization at C(20) of the spirosteradienes yields the (20S)-counterparts **16a**/**16b** *via* the intermediate $\Delta^{8,17(20)}$-steroid by a reversible 13(17)-double bond migration. The energies of these $\Delta^{8,17(20)}$-spirosteroids are several kcal higher than those of the corresponding $\Delta^{8,13(17)}$-steroids. Therefore, if we consider that the product distributions observed at longer than 130 h represent equilibrium ratios, the slight predominance of (20R)-isomers of $\Delta^{8,13(17)}$-spirosteroids and the absence of $\Delta^{8,17(20)}$-spirosteroids among the reaction products fit fairly well with the thermodynamic stabilities.

Conclusion. – The rearrangement reactions of diunsaturated steroids in the presence of anhydrous TsOH/AcOH at 70° proceed by intermediate allylic or tertiary carbocations yielding C=C bond migration products. However, a backbone rearrangement of one of these carbonium ions (*e.g.* **B**) by ring contraction leads to $\Delta^{8,13(17)}$-spirosteroids which subsequently epimerize at C(20). Evolution of the reaction products with time, as well as the product distribution at equilibrium, are in agreement with the calculated stability values. These rearrangement products are expected to be found in sediments as biomarkers for sterols containing two C=C bonds in the skeleton.

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Experimental Part

General. Solvents (*Fluka* or *Merck, puriss.*) were used without further purification. THF was freshly distilled from Na/benzophenone under N_2. Reactions were run under N_2. HPLC: normal-phase *Merck LiChrospher Si 60* (10 μm) column (250 × 10 mm) or reversed phase *Merck LiChrosorb RP-18* (7 μm) column (250 × 10 mm), with hexane *LiChrosolv®* at 2.5 ml/min and MeOH *Lichrosol®* at 4 ml/min, resp., *Waters-RI-401* differential refractometer or *Merck-L-4500* diode-array (180–800 nm) detector, resp. GLC: *Carlo-Erba* gas chromatograph *GC 5160*; fused silica capillary *SE-30* (30 m × 0.32 mm); He (70 kPa); 1 min at 60°, 15°/min to 230°, 2°/min to 260°, 5°/min to 300°. UV: *Merck-L-4500* diode array or *Kontron Instruments Uvikon®-810P* spectrophotometer, λ_{max} in nm. ^{1}H- and ^{13}C-NMR, H,H-COSY.DQF, H,C-COSY, and NOESY: *Bruker AMX 400* or *Bruker AMX-2 600* at 9.4 or 14.1 Tesla, in $CDCl_3$; chemical shifts δ in ppm rel. to $SiMe_4$. GLC/MS: *VG Masslab Trio-2* coupled with a *Hewlett-Packard-5890* gas chromatograph. MS: at 70 eV, source temp. 190°.

$LiAlH_4$ Reduction of Toluene-4-sulfonate **10**. A mixture of cholesta-5,7-diene-3β-yl toluene-4-sulfonate (**10**; 330 mg, 0.6 mmol) and $LiAlH_4$ (1 g, 26.4 mmol) in THF (200 ml) was warmed at 70° for 4 h. After cooling to r.t., excess of $LiAlH_4$ was destroyed by dropwise addition of H_2O. Then 6N HCl was added (→clear soln.), the mixture extracted with Et_2O, the extract washed with H_2O and sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. Normal-phase HPLC of the residue (110 mg, 49%) afforded pure **11**.

NaI/Zn Reduction of Toluene-4-sulfonate **10**. A mixture of **10** (139 mg, 0.26 mmol), NaI (193 mg, 1.3 mmol), and Zn powder (168 mg, 2.6 mmol) in dimethoxyethane (5 ml) was warmed to reflux for 4 h. The mixture was filtered and the filtrate poured into H_2O (5 ml). Extraction with pentane, followed by washing with sat. aq. NaCl soln., drying (Na_2SO_4), and evaporation gave 65 mg of oily residue. Normal-phase HPLC gave a first fraction (11 mg) containing two components of mol. wt. 368 (ratio *ca.* 1:3) and a second one (25 mg) of pure **12**. Reversed-phase HPLC of the first fraction yielded **13b** and **13a** in this order of elution.

Acid-Catalysed Rearrangements of $\delta^{6,8(14)}$-Steroids **13a** *and* **13b**. In a typical experiment, **13** (5 mg) in 0.5 ml of anh. TsOH/AcOH (3% *w/v*) [5] was heated in a mini-vial (1 ml; *Alltech*) at 70° for a given time. Dilution with H_2O (10 ml), extraction with CH_2Cl_2, followed by washing with sat. aq. $NaHCO_3$ soln. and drying yielded a mixture of products which was analysed by GC/MS. $\Delta^{8,14}$-Steroid **14b** and $\Delta^{8,13(17)}$-spirosteroid **15b** could be isolated by reversed-phase HPLC from the 3 h reaction product of **13b**.

3,5-Cyclocholest-7-ene (**11**). ^{1}H- and ^{13}C-NMR: *Table 1*. EI-MS: 368 (100, $M^{+\cdot}$), 363 (42, [M – Me]$^+$), 327 (11), 311 (14), 274 (10), 255 (43, [M – (side chain)]$^+$), 253 (21), 228 (17), 213 (41, double cleavage of C(13)–C(17) and C(14)–C(15)), 201 (24), 145 (56).

3,5-Cyclocholesta-6,8(14)-diene (**12**). UV (MeOH): 261. ^{1}H- and ^{13}C-NMR: *Table 1*. MS: 366 (19, $M^{+\cdot}$), 253 (100, [M – (side chain)]$^+$), 239 (7), 227 (10), 211 (9), 199 (43).

5α-Cholesta-6,8(14)-diene (**13a**). UV (MeOH): 252. ^{1}H- and ^{13}C-NMR: *Table 1*. MS: 368 (21, $M^{+\cdot}$), 353 (25), 283 (5), 271 (4), 255 (100, [M – (side chain)]$^+$), 241 (7), 229 (18), 214 (9), 213 (8), 201 (35).

5β-Cholesta-6,8(14)-diene (**13b**). UV (MeOH): 249. ^{1}H- and ^{13}C-NMR: *Table 1*. MS: 368 (20, $M^{+\cdot}$), 353 (32), 283 (3), 271 (4), 255 (100, [M – (side chain)]$^+$), 241 (7), 229 (23), 214 (10), 213 (8), 201 (47).

5α-Cholesta-8,14-diene (**14a**). UV (MeOH): 249.6. MS: 368 (64, $M^{+\cdot}$), 353 (100), 325 (5), 312 (5), 283 (3), 255 (26, [M – (side chain)]$^+$), 241 (23), 240 (29), 239 (10), 227 (5), 225 (6), 213 (9), 199 (1).

5β-Cholesta-8,14-diene (**14b**). UV (MeOH): 249.6. ^{1}H- and ^{13}C-NMR: *Table 1*. MS: 368 (54, $M^{+\cdot}$), 353 (100), 312 (3), 255 (26, [M – (side chain)]$^+$), 241 (26), 240 (33), 239 (16), 227 (6), 225 (5), 213 (11), 199 (12).

(20R)-12(13→14)-abeo-*5α-Cholesta-8,13(17)-diene* (**15a**). UV (MeOH): < 200. MS: 368 (25, $M^{+\cdot}$), 353 (93), 283 (33, allylic cleavage of C(22)–C(23)), 271 (5), 255 (100, [M – (side chain)]$^+$), 241 (5), 227 (4), 205 (17), 202 (30), 187 (21), 173 (18), 159 (21), 145 (29), 121 (35), 105 (38), 91 (41).

(20S)-5-12(13→14)-abeo-*5α-Cholesta-8,13(17)-diene* (**16a**). UV (MeOH): < 200. MS: 368 (22, $M^{+\cdot}$), 353 (83), 283 (34), 271 (4), 255 (100, [M – (side chain)]$^+$), 241 (5), 227 (3), 205 (16), 202 (17), 187 (19), 173 (16), 159 (20), 145 (21), 121 (34), 105 (36), 91 (38).

(20R)-12(13→14)-abeo-*5β-Cholesta-8,13(17)-diene* (**15b**). UV (MeOH): < 200. ^{1}H- and ^{13}C-NMR: *Table 1*. MS: 368 (44, $M^{+\cdot}$), 353 (97), 325 (3), 312 (3), 283 (62), 255 (100, [M – (side chain)]$^+$), 241 (4), 227 (6), 215 (8), 205 (12), 202 (44), 187 (21), 173 (17), 159 (22), 145 (30), 121 (32), 105 (49), 91 (41).

(20S)-12(13→14)-abeo-*5β-Cholesta-8,13(17)-diene* (**15b**). UV (MeOH): < 200. MS: 368 (35, $M^{+\cdot}$), 353 (87), 325 (3), 312 (2), 283 (54), 255 (100, [M – (side chain)]$^+$), 241 (5), 227 (6), 215 (8), 205 (10), 202 (41), 187 (19), 173 (17), 159 (20), 145 (29), 121 (31), 105 (47), 91 (39).

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