trace of the triplet state cannot be recorded by EPR, NMR, or static magnetic susceptibility. In favor of the assumption of paired spin of the two radicals in $Pd(A^*H)_2$ is the fact that when excess AH_2 is added to the $Pd(A^*H)_2$ solution, the number of radical particles increases sharply (30-35% of the starting $Pd(A^*H)_2$ is recorded); this can be explained by the replacement of one of the A^*H particles in $Pd(A^*H)_2$ and by AH particle.

Thus, the oxidations of palladium(II) and nickel(II) chelates [2] with HAO proceed in like manner; they are accompanied by oxidative dehydrogenation of the sterically hindered coordinated HAO anions via the N–H bond, and formation of intermediate paramagnetic complexes of metal with nitroxyl radical anions.

CONCLUSIONS

1. When oxidants act on palladium(II) chelates with 1,2-hydroxylaminooximes, oxidative hydrogenation occurs via the N–H bond of the coordinated ligands.

2. It has been shown by EPR that an intermediate in the oxidation is a palladium(II) complex that contains a nitroxyl radical.

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TRANSFORMATIONS OF STEROIDS

COMMUNICATION 139. SYNTHESIS AND REARRANGEMENT OF 8, 14,-EPOXY-12-KETO-CHOLANIC ACIDS

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UDC 542.91+542.952.1:547.92

1,2-Shifts of methyl groups in steroid molecules and triterpenoids, processes such as anionotropic rearrangements (Westphalen, Wagner-Meerwein, "backbone," and others) [1], originate with the regeneration of cation centers adjacent to the carbon atom attached to the migrating group and are controlled by the kinetics and the stereochemistry. Rearrangements proceed under those circumstances in which the carbonium ion is formed by ionization of electronegative substituents (such as I), protonization of olefin bonds, and acid catalyzed opening up of epoxy rings. In particular the reactions of steroid epoxides with Lewis acids [2], in which the formation of cationoid centers, occurring after the rupture of the oxygen ring induces subsequent 1,2-shifts of CH_3 groups and H atoms in the entire skeleton were thoroughly studied. In case of the presence of carbonyl groups in the β-position to the epoxy ring, for example, with 7-keto-9(11)-epoxides, stabilization of the carbocation takes place [3, 4], under the reaction conditions which leads to keeping the rearrangement within the A/B or C/D parts of the molecule depending on the configuration of the oxygen ring. Our investigations showed that replacing the carbonyl group in ketoepoxides and ketoepimines drastically alters the regio- and stereoselectivity of the course of the reactions [5]. Naturally, it would be significant to examine the impact of such a replacement on the course of the 1,2-shift reaction, in particular, in the case of the 18-methyl group, in which its transfer to the 14 position could have preparative importance. As a model we used the readily available cholic acid making it possible to synthesize the 8,14-epoxy-12-keto grouping.

In the present communication we describe the synthesis of 8,14α- and 8,14β-epoxy-12-ketones and their rearrangement under the influence of Lewis acids and protons. The synthesis of model compounds was carried

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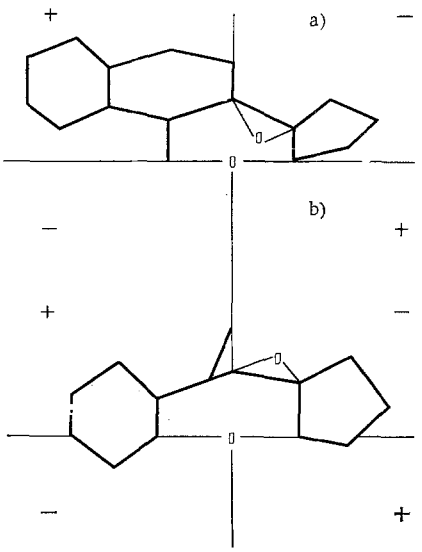
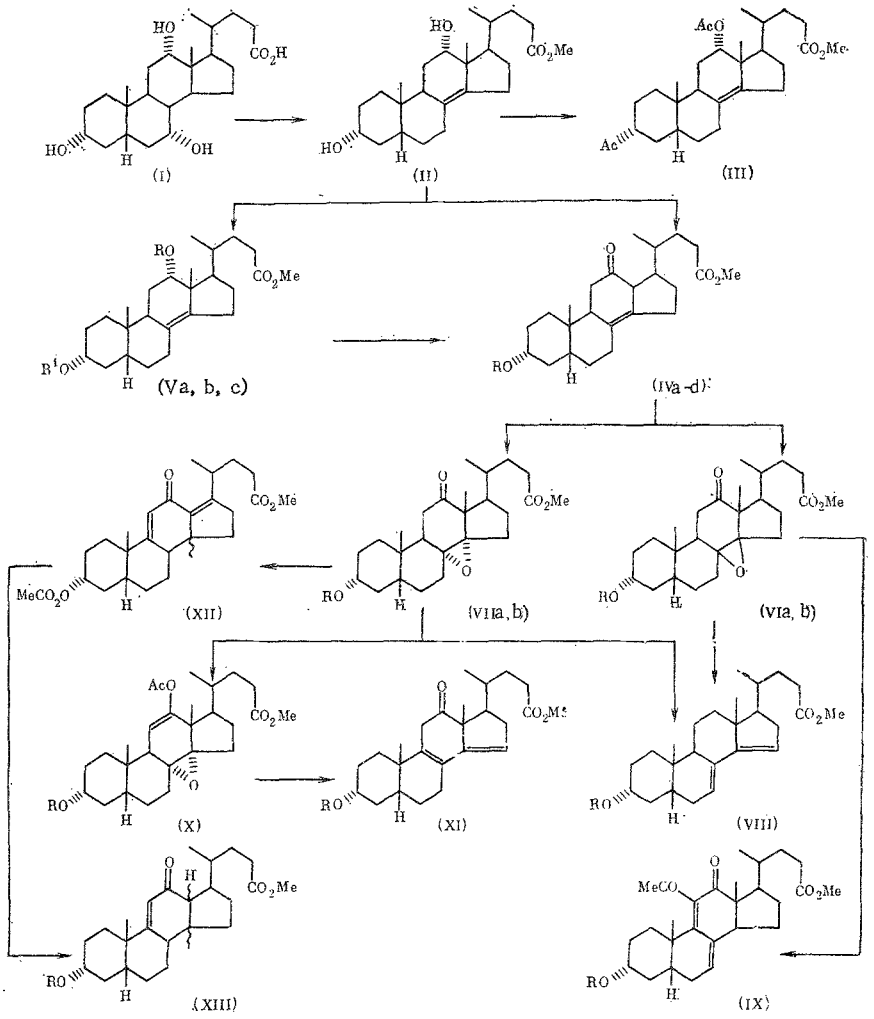


Fig. 1. Octant projections of 8,14β-(VI) (a), and 8,14-α epoxides (VII) (b).

out according to the following scheme: The dehydration of cholic acid (I) by means of $ZnCl_2$ with subsequent esterification by CH_2N_2 leads to the methyl ester of apocholic acid (II) in high yield, also characterized in the form of the 3α,12α-diacetate(III). Formed in this way as a minor product was the methyl ester of 3,12-dihydroxychol-7-enoic acid [6], becoming predominant on decreasing the reaction time for dehydration from 2.5 h to 40-50 min, in which instance the separation of the Δ^7-isomer becomes difficult. For preparation of the 12-ketoderivative of methyl apocholate we took advantage of the tendency of the 12-α-hydroxy group to oxidize easily in comparison to the 3-α-hydroxy group (as is known, in the 5β series this increases in the order 3α < 12α < 7α) [7]. However, the yield of (IVa), characterized in the form of the 3-accetate (IVb), seemed lower than expected. Better results were obtained by preliminary protection of the 3-position. Selective acylation at C-3 was attained by using chlorocarbonic ester [8]. Oxidations of (Va-c) by the Jones method with satisfactory yields led to the formation of the corresponding 12-ketones (IVb-d), among which (IVd) has physical constants which coincide with those described in [9]. For epoxidation of the $\Delta^{8(14)}$bond various reagents were used (H_2O_2 with PhCN, t-BuOOH with $MoCl_5$ [10, 11]), peracids: monoperphthalic acid in CH_2Cl_2, chloroperbenzoic acid in ether, among which the m-chloroperbenzoic acid seemed the most successful. Epoxidation in all instances was not stereospecific and the 8β,14β-(VI)- and 8α,14α-(VII)-isomers were formed in a 9:1 ratio, and separated chromatographically. Structures of both isomers were demonstrated by physicochemical methods. The stereochemistry of (VI) and (VII) were assigned by infrared and circular dichroism and PMR spectral data [12]. For consideration of models of α- and β-epoxyketones (VI) and (VII) on the basis of the octant rule in the case of the β-epoxide (with rings A, B, C in the chair form) the situation arises that when the A/B rings are located in the upper left octant then the sign of the Cotton effect should be positive. The epoxy ring in the case of the β-isomer falls within the upper right octant but since the octant rule for oxides is the reverse of the rule for ketones the positive value of Δε in comparison with the usual 12-keto-14β-steroids is increased, which agrees with the experiment (λ_{max} = 287 nm, Δε = + 1.47). In the case of the α-epoxide (VII) the A/B rings project partially in the upper left octant and the positive contribution is somewhat invalidated by the contribution of rings C/D located in the upper right octant. α-Epoxide rings bring in a positive contribution to the Cotton effect by the $n \rightarrow \pi^*$ transitions of the C=O chromophore, thus for the α-isomer (VII) a small value is expected for the Cotton effect (λ_{max} = 292.5, Δε = + 0.64) (Fig. 1). The PMR spectra of (VI) and (VII) are different in the chemical shifts of the 18-CH_3 protons in that the chemical shift of the β-isomer is substantially displaced in a weak field, as has been observed with the 5β,14β-steroids in comparison with their 5β,14α-analogs (δ 1.17 and 1.07 ppm, respectively).

We have studied the action of proton acids (HCl, HClO, CF_3COOH), and Lewis acids ($SnCl_4$, $TiCl_4$, $BF_3 \cdot Et_2O$) on both isomers and found that the 8β,14β (VI) isomer is significantly less stable to electrophilic attack. Even in AcOH at 20°C in the course of two days it is converted to the 7,14-diene, (VIII) whereas the α isomer is stable under analogous conditions. In the presence of mineral acids it is also converted to the diene (VIII) which is verified by the characteristic absorption in the UV spectrum [13] (λ_{max} = 250 nm, ε = 6055) and the presence of a signal of vinyl protons (δ 5.46, 5.8 ppm) in the PMR spectrum. The reaction capability of the β-epoxide was studied under the conditions of the backbone rearrangement [2, 3] under the influence of BF_3 in benzene and in Ac_2O. In benzene the diene (VIII) is formed. In acetic anhydride along the opening of the epoxide ring, C-acylation occurred at C^{11}. Evidently, the acetyl ion attacks the 11-position of the enolate ion with the formation of the β-diketone (IX) [14].



R=H(IVa), Ac(IVb), COOMe (IVc), (VIa), (VIIa), (VIII) — (XI), (XIII);
R=H, R^1=COOMe (Va); R=R^1=COOMe (Vb); R=H, R^1=COOEt (Vc).

Structure (IX) showed the typical diene absorption in the UV spectrum of λ_{max} = 280 nm, ε = 14,500, the presence of signals of a vinyl proton in a conjugated system and acetyl next to a double bond (δ 5.8; 2.17 ppm), in the ^{13}C NMR spectrum the presence of signals from four vinyl carbons, in which one is secondary, and two carbonyls; characteristic fragmentation in the mass spectrum: M − 43(457), M − 43 − 76 etc, (see Experimental). It is interesting that under the same conditions the α-epoxide (VII) is completely stable, except only that enolization of the 12-carbonyl takes place as a result of which the epoxy acetate (X) forms, the treatment of which with $HClO_4$ and AcOH yields the diene (XI). The 8,14-diene system is linked with the appearance of characteristic absorption in the UV spectrum (λ_{max} = 245 nm, ε = 12,156), the presence in the PMR spectrum of a signal of one vinyl proton (δ = 5.5 ppm), and displacement in the weaker field of the C^{18} CH_3 and C^{19} CH_3 proton signals in comparison with 7,14-dienes (VIII) [15]. Evidently, first of all the ring is opened in (X) with formation of a conjugated bond system and then the shift of the enol acetate to the 12-ketone. In contrast to the β-epoxide (VI) this stereoisomer(VII) reacts differently with BF_3 in benzene. Even after 15 min the hydroxyenone is formed, which after longer exposure is converted to the rearranged product (XII). The reaction is evidently initiated by attack by the BF_3 on the epoxide; formation of the carbocation at C^{14} is blocked by the 12-carbonyl and proceeds by migration of the CH_3 group from position 13 to 14. The structure of (XII) is verified by the UV absorption, characteristic of cross conjugated dienes (λ_{max} = 333 nm, ε = 843, 282 nm, ε = 4709, 233 nm, ε = 3965). In the PMR spectrum the signal of one vinyl of an α-β-unsaturated ketone (δ = 5.95 ppm) a three proton doublet at δ = 0.93 ppm with a spin–spin splitting of J = 8 Hz from the 21-CH_3 and two singlets, δ = 1.15 and 1.23 of the angular methyl groups are found. In the mass spectrum the molecular ion peak (m/z 458), and the intensive peak (m/z 343) caused by the open side chain characteristic of the $\Delta^{13(17)}$ system [3] $[M - 115]^+$. Diene (XII) appears stable to reduction by $NaBH_4$ and $NaBCNH_3$. By hydrogenation over PtO_2 in AcOH the 13(17) bond is reduced. The presence of the α-β-unsaturated ketone in compound (XIII) is verified

by the absorption characteristic of the Δ^9-12 ketosystem in the UV spectrum at λ_{max} 227 nm [16]. In the mass spectrum the molecular ion peak was at m/z 460. It is known [16] that 12-keto-5β-chol-9(11)-enate is extremely difficult to hydrogenate, and the mixtures of saturated and starting ketones formed are practically inseparable. We have shown that the ketone in the (XIII) system is incapable of reacting, in that on attempting to prepare the tosyl hydrazone in acetic acid, the starting material remained after 24 h, and a longer exposure led to the formation of condensation products.

EXPERIMENTAL

Melting point was determined on a Kofler block. IR spectra were measured on a UR-20 spectrometer in $CHCl_3$; UV spectra on the Unicam SP-700 apparatus in EtOH. Mass spectra were recorded on a Varian MAT CH-6 mass spectrometer with direct introduction of samples into the ionization chamber and an ionization potential of 70 eV. PMR spectra were measured on a Tesla BS-497 apparatus, internal standard TMS in $CDCl_3$. Circular dichroism spectra were measured on the Dichrograph-3 (Joben Ivon) instrument at 20-23°C, 1 mg/ml in MeCN, cuvette path length 0.1 cm. For TLC Silufol UV-254 sheets were used in a 2:1 benzene–EtOAc system. Development was by spraying with a 2% solution of $Ce(SO_4)_2$ in 2 N H_2SO_4 with subsequent heating. Separation of the mixture was carried out on SiO_2 5/40 μm, and Al_2O_3 (activity II) in a nitrogen atmosphere.

Methyl Ester of 3α-Methoxycarbonyloxy-5β-chol-8(14)-en-12α-ol-24-oic Acid (Va). To a solution of 4 g of (II) with a mp of 82-84°C [2] in 100 ml benzene (dried and double distilled) was added 4 ml of pyridine and 3 ml of the methyl ester of chlorocarbonic acid in 20 ml of the benzene at 10-15°C. After 18 h it was treated with 5 ml of water, the benzene layer separated, washed with 5% HCl, and with water, dried over anhydrous $MgSO_4$, the solvent evaporated. The residue (4.5 g) was chromatographed on SiO_2 using a benzene–ether system. Yield: 1) 3.2 g of (Va) in the form of a colorless oil, which crystallized on standing, mp 117-120°C (from petroleum ether). IR spectrum (ν, cm^{-1}): 3520, 1730, 1260. Mass spectrum (m/z): 462 (3, M^+), 444 (40, M−18), 386 (21, −76), 368 (30, M − 18 − 76), 329 (63, M − 18 − 115), 253 (100, M − 18 − 76 − 115). PMR spectrum (δ, ppm), 0.85, 0.75 s (9H, 18-CH_3, 19-CH_3, 21-CH_3), 3.55 s (3H, OCH_3), 3.63 s (3H, OCH_3), 3.78 m (1H, 3β-H). 2) 0.65 g of (Vb), R_f 0.88. Under the same conditions (Vc) is obtained with the same R_f as (Va).

Methyl Ester of 3α-Methoxycarbonyloxy-5β-chol-8(14)-en-12-on-24oic Acid (IVc). To a solution of 3.2 g of (Va) in 50 ml acetone, cooled to 0°C a solution of CrO_3 in H_2SO_4 (10% excess) was added with stirring. After disappearance of the (Vb) (TLC) the solution was decanted into 100 ml of water and extracted with $CHCl_3$. The residue was washed with $CHCl_3$, the combined extracts washed with water, dried and solvent evaporated. There was obtained 3.2 g of (IVc) mp 176-178°C. IR spectrum (ν, cm^{-1}) : 1735, 1710, 1270, 1260. Mass spectrum (m/z): 460 (19, M^+), 442 (6, M − 18), 428 (6, M − 32), 384 (54, M − 76), 366 (16, M − 18 − 76), 351 (23), 269 (30, M − 76 − 115), 251 (38), 229 (100). PMR spectrum (δ, ppm), 0.86 d (3H, 21-CH_3), 1.01 s (3H, 18-CH_3), 120 s (3H, 19-CH_3), 3.60 s (3H, OCH_3), 3.69 s (3H, OCH_3), 4.5 m (1H, 3β-H). Under the same conditions (IVd) was obtained, mp 119-121 (see [2]). The 3α-acetate (IVb) was obtained by oxidizing 850 mg of (II) in 15 ml AcOH by means of 700 mg K_2CrO_7 in 1 ml of water. After treatment with water, extraction, drying and evaporating the solvent the ketone was treated with 2 ml Ac_2O in 5 ml pyridine for 18 h, followed by chromatographic purification on SiO_2 using the ether–petroleum ether system which yielded 470 mg (IVb) mp 117-120°C (from benzene–petroleum ether). IR spectrum (ν, cm^{-1}) 1735, 1710, 1270. Mass spectrum (m/z): 444 (22, M^+), 384 (43, M − 60), 366 (29, M − 18 − 60), 351 (40), 311 (50), 269 (50, M − 60 − 115), 251 (100, M − 18 − 60 − 115).

Methyl Ester of 3α-Methoxycarbonyloxy-8α, 14α- and 8β,14β-epoxy-5β-chol-12-on-24-oic Acid (VI) and (VII). A mixture of 3 g of (IVc) in 150 ml ether and 1.5 g chloroperoxybenzoic acid was kept at 20°C for 48 h, washed with 10% Na_2CO_3, and with water, dried, and the solvent evaporated. The residue was separated chromatographically on Al_2O_3 using benzene. Yield: 1) 0.25 g of the α-epoxide (VII) R_f 0.75. Mass spectrum (m/z): 476 (96, M^+), 458 (24, M − 18), 444 (32, M − 32), 400 (100, M − 76), 382 (M − 18 − 76, 48), 267 (54, M − 18 − 76 − 115). PMR spectrum (δ, ppm): 0.85 d (3H, 21-CH_3), 1.07, 1.23 s (6H, 18-CH_3, 19-CH_3), 3.60 s (3H, OCH_3), 3.75 s (3H, OCH_3), 4.50 m (1H, 3-H). 2) 2.23 g β-epoxide (VIa), mp 163-165°C (from petroleum ether). IR spectrum of both isomers (ν, cm^{-1}): 1730, 1710, 1260. Mass spectrum (m/z): 476 (57, M^+), 400 (85, M − 76), 382 (22, M − 18 − 76), 285 (100, M − 76 − 115). PMR spectrum (δ, ppm): 0.85 d (3H, 21-CH_3), 1.17, 1.23 s (6H, 18-CH_3, 19-CH_3), 3.58 s (3H, OCH_3), 3.68 s (3H, OCH_3), 4.53 m (1H, 3-H). The 3-acetates of the α- and β-epoxides and the 3-ethoxycarbonyloxy- derivatives were obtained in this same way.

Methyl Ester of 3α-Methoxycarbonyloxy-5β-chol-7,14-dien-12-on-24-oic Acid (VIII). a) To a solution of 300 mg of the β-epoxide (VIa) in 20 ml of benzene was added 0.03 ml of $BF_3 \cdot Et_2O$. After 10 min (TLC) the mixture was washed with water, dried and the solvent evaporated. There was obtained 290 mg of (VIII), mp 138-140°C (petroleum ether). IR spectrum (ν, cm^{-1}): 1730, 1710, 1640, 1600, 1290. UV spectrum (λ_{max}, ε): 250 (6055). Mass spectrum (m/z): 458 (18,M^+), 440 (7, M − 18), 382 (18, M − 76), 267 (100, M − 76 − 115). PMR spectrum (δ, ppm): 0.85 d, 0.87, 1.08 s (9H, 21-CH_3, 18-CH_3, 19-CH_3), 3.58 s (3H, OCH_3), 3.65 s (3H, OCH_3), 4.52 m (1H, 3-H), 5.46 m, 5.80 m (2H, 7-H, 15-H).

b) To a solution of 300 mg of (VIa) in 10 ml acetone was added 0.06 ml of $HClO_4$, after 18 h it was treated with 50 ml of water, extracted with $CHCl_3$, the extract washed with 10% $NaHCO_3$ dried and the solvent evaporated. There was obtained 250 mg of (VIII), mp 139°C.

Methyl Ester of 11-Acetyl-3α-methoxycarbonyloxy-5β-chola-7,9(11)-dien-12-on-24-oic Acid (IX). To a solution of 600 mg of the β-epoxide (VIa) in 20 ml of Ac_2O was added 0.5 ml $BF_3 \cdot Et_2O$. After 45 min (TLC) 20 ml of pyridine was added and the solution carefully poured into 100 g of ice water, extracted with ether, washed three times with solutions of 5% HCl, $NaHCO_3$, and water, dried and the solvent evaporated. After purifying the residue chromatographically on Al_2O_3 using ether–benzene system 120 mg of (IX) was obtained, mp 146-147°C (from petroleum ether–benzene). IR spectrum (ν, cm^{-1}): 1735, 1660, 1640, 1600, 1280. UV spectrum (λ_{max}, nm, ε): 280 (14,500). Mass spectrum (m/z): 500 (11, M^+), 457 (30, M − 43), 381 (20, M − 43 − 76), 343 (100, M − 42 − 115), 267 (70, M − 42 − 76 − 115). PMR spectrum (δ, ppm): 0.83 d, 0.94, 1.19s, (9H, 21-CH_3, 18-CH_3, 19-CH_3), 2.17 s (3H, $COCH_3$), 3.64 s (3H, OCH_3), 3.72 s (3H, OCH_3), 4.59 m (1H, 3-H), 5.8 m (1H, 7-H).

Methyl Ester of 12-Acetoxy-3-methoxycarbonyloxy-8α-14α-epoxy-5β-chol-11(12)-en-24-oic Acid (X). From 200 mg of the α-epoxide (VIIa) under the reaction conditions described above with $BF_3 \cdot Et_2O$ in Ac_2O there was obtained 160 mg of the enol acetate (X), R_f 0.27. IR spectrum (ν, cm^{-1}): 1730, 1700, 1600, 1280-1260. UV spectrum (λ_{max}, nm); 206. Mass spectrum (m/z): 518 (2, M^+), 458 (73, M − 60), 382 (29, M − 60 − 76), 267 (100, M − 60 − 76 − 115). PMR spectrum (δ, ppm): 0.84 d (3H, 21-CH_3), 1.03, 1.15 s (6H, 18-CH_3, 19-CH_3), 2.02 s (3H, OAc), 3.62 s (3H, OCH_3), 3.72 s (3H, OCH_3), 4.57 m (1H, 3-H), 5.16 m (1H, 11-H).

Methyl Ester of 3α-Methoxycarbonyloxy-5β-chola-8,14-dien-12-on-24-oic Acid (XI). To a solution of 150 mg of (X) in 5 ml AcOH was added 0.15 ml of concentrated HCl. After the standard treatment (18 h, 20°C) and chromatographing on Al_2O_3 using the ether–petroleum ether system there was obtained 90 mg (XI), mp 149-151°C. IR spectrum (ν, cm^{-1}): 1730-1710, 1640, 1580, 1290-1270. UV spectrum (λ_{max}, nm, ε): 245 (12,156), 294 (711). Mass spectrum (m/z): 458 (18, M^+), 382 (30, M − 76), 367 (23, M − 76 − 15), 267 (100, M − 76 − 115). PMR spectrum (δ, ppm): 0.94 d, 1.16, 1.26 s (6H, 21-CH_3, 18-CH_3, 19-CH_3), 3.67 s (3H, OCH_3), 3.74 s (3H, OCH_3), 4.62 m (1H, 3-H), 5.50 m (1H, 15-H).

Methyl Ester of 3α-Methoxycarbonyloxy-5β-chol-9(11),13(17)-dien-14ξ-methyl-12-on-24-oic Acid (XII). To a solution of 300 mg of the α-epoxide (VIIa) in 20 ml of benzene was added 0.3 ml of $BF_3 \cdot Et_2O$, after 3 h (TLC) it was treated with water and extracted with ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and the solvent evaporated. After chromatographing the residue on Al_2O_3 using the ether–petroleum ether system there was obtained 190 mg of noncrystalline diene (XII), R_f 0.79 (benzene–EtOAc, 2:1). IR spectrum (ν, cm^{-1}): 1730, 1690, 1650, 1600, 1260. UV spectrum (λ_{max}, ε): 282 (4700), 233 (4000). Mass spectrum (m/z): 458 (16, M^+), 343 (100, M − 115), 327 (20), 267 (44, M − 76 − 115). PMR spectrum (δ, ppm): 0.93 d 1.15, 1.24 s (9H, 21-CH_3, 18-CH_3, 19-CH_3), 3.63 s (3H, OCH_3), 3.72 s (3H, OCH_3), 4.58m (1H, 3-H), 6.00 m (1H, 11-H).

Methyl Ester of 3α-Methoxycarbonyloxy-5β-chol-9(11)-en-14ξ-methyl-12-on-24-oic Acid (XIII). Compound (XII) (100 mg) was hydrogenated in AcOH over 30 mg PtO_2 for 24 h until H_2 absorption ceased (no change in the TLC). The catalyst was filtered off, the solution treated with water and extracted with ether. The extract was washed with a 5% solution of $NaHCO_3$ and with water, dried, the solvent evaporated. After chromatographing the residue on Al_2O_3 using the ether–petroleum ether system 50 mg of the enone (XIII) were separated as an oil. R_f 0.79 (benzene–EtOAc). IR spectrum (ν, cm^{-1}): 1730, 1690, 1620, 1260. UV spectrum (λ_{max}, nm, ε) 230 (4300). Mass spectrum (m/z): 460 (85, M^+), 384 (100, M − 76), 269 (23, M − 76 − 115). PMR spectrum (δ, ppm): 5.7 m (1H, 11-H).

CONCLUSIONS

1. We have carried out the syntheses of 8α, 14α- and 8β, 14β-epoxy-12-ketocholanic acids and their 3-acyl derivatives.

2. β-Epoxides by the action of proton acids and Lewis acids are converted to the 7,14 choladienes, and by the action of boron trifluoride in acetic anhydride, to the product acylated at C^{11}, α-epoxides under proton acid conditions yield 8,14-dienes, and under "backbone" rearrangement conditions with boron trifluoride in benzene, to the rearrangement product, the methyl ester of 3α-methoxycarbonyloxy-5β-chola-9(11), 13(17)-diene-14ξ-methyl-12-on-24-oic acid. The $\Delta^{13(17)}$ bond was reduced by hydrogenation over Adams catalyst.

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