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CIRCULAR DICHROISM OF SOME CYCLOPROPANE RING CONTAINING 1,3-CYCLO-5,10-SECO-STEROIDAL KETONES[1]

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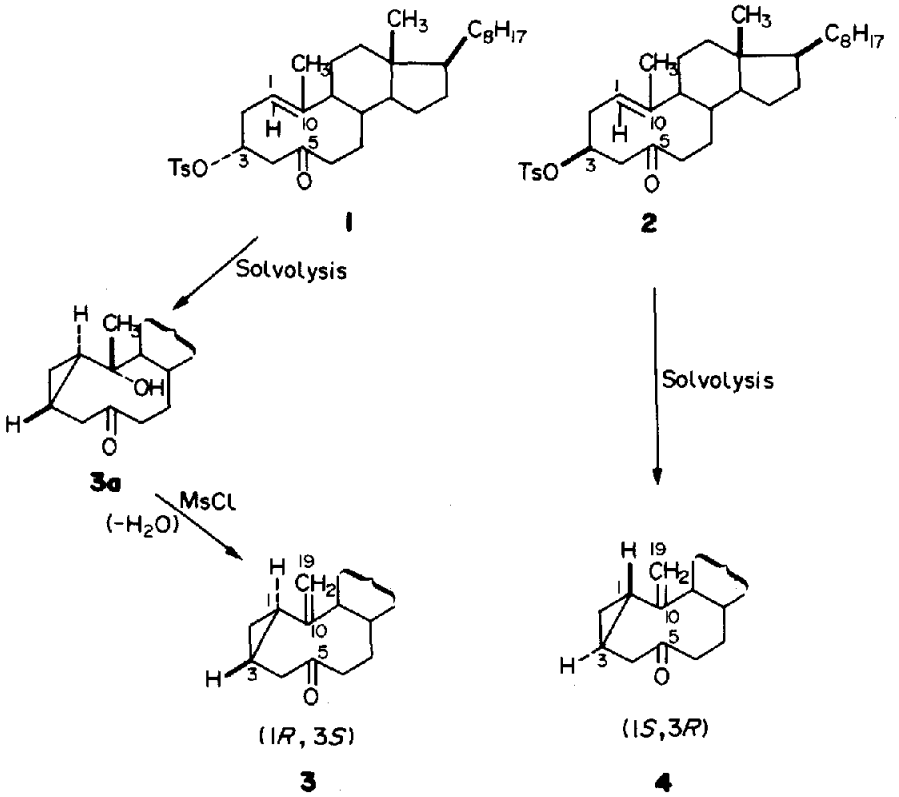
Abstract—Circular dichroism of the rearranged keto steroids **3** and **4**, containing a condensed three and nine-membered ring system, shows that the conformation of the nine-membered ring is the same in solution as in the crystal; reduction of the keto group does not change this situation. CD also indicates that epimerization at C(5) in the pair **7**/**8** and the pair **11**/**12** leaves the cyclononanone ring conformation unchanged.

As previously reported,[2,3] solvolysis of the epimeric (*E*)-3α- and (*E*) - 3β - tosyloxy - 5,10 - seco - cholest - 1(10) - en - 5 - ones **1** and **2** in buffered acetone–water (90:10 v/v) solution at reflux proceeds with homoallylic π-bond participation and internal C(1)–C(3) bond formation, affording (among other products) the diastereomeric 1,3 - cyclo - 5,10 - seco - steroidal 5-ketones **3** (upon dehydration)§ and **4** (direct product), respectively (Scheme 1), which both contain a bicyclo[7.1.0]-decane system instead of the two 6-membered rings A and B.



Scheme 1.

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§The primarily formed product from the 3α-tosylate **1** being, actually, the 10-methyl-10-hydroxy-1,3-cyclo derivative **3a**, which can readily be dehydrated (by means of mesyl chloride) to the corresponding olefinic compound **3**.[3]

Since, owing to the conformational mobility of the 9-membered ring, configurational assignments at C(1) and C(3) by the usual physical methods (CD, ^{1}H- and ^{13}C-NMR spectra) proved to be impossible, the *trans* 1*R*,3*S*-configuration of the cyclopropane derivative **3** (obtained from the 3α-tosylate **1**) and the *trans* 1*S*,3*R*-configuration of the diastereomeric ketone **4** (produced from the 3β-tosylate **2**) were established by X-ray analysis.[4] It was also shown that the solid-state conformation of the 9-membered ring in compound **3** closely approximates to a twist–chair–chair (C_2) form,[5] with the two-fold axis of symmetry passing through C(8) and the mid-point of the C(3)–C(4) bond (**3-A**, Scheme 2), while the corresponding 9-membered ring in the cyclopropane derivative **4** is best considered as a distorted chair–boat (C_s) form,[5] in which a mirror plane of symmetry passes through C(9) and the mid-point of the C(4)–C(5) bond (**4-B**, Scheme 2).

In the present paper, CD spectra of these 10(19)-unsaturated 1,3-cyclo-5-ketones **3** and **4**, as well as of the derived compounds, i.e. the 10(19)-olefinic 5-acetates **9** and **10**, and also of the corresponding 1,3 - cyclo - 10 - keto - 5 - acetates **7**, **8**, **11** and **12** (Scheme 3), are discussed in order to deduce the conformation(s) of the 9-membered ring in these modified steroid molecules in solution.

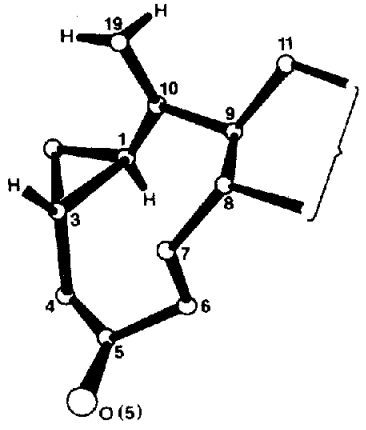
Compounds **7–12** were prepared from the 5-ketones **3** and **4** by the reaction sequences outlined in Scheme 3. The configuration at C(5) in **9** and **10**, and also in **11** and **12**, follows from the fact that the 5-acetate **9**, upon acetolysis, undergoes opening of the 3-membered ring to give the known (*E*) - 3β,5α - diacetoxy - 5,10 - seco - 1(10) - cholesten - 5 - one **13**,[6] while the acetate **10**, under similar experimental conditions, produces the epimeric compound (*E*) - 3β,5β - diacetoxy - 5,10 - seco - 1(10) - cholesten - 5 - one **14**.[7] By comparing ^{1}H-NMR spectral data (Table 1), it was possible to correlate the stereochemistry at C(5) of the 10 - keto - 5 - acetates **7** and **8** (in the 1*R*,3*S*-series) with that of the respective compounds **11** and **12** (in the 1*S*,3*R*-series).

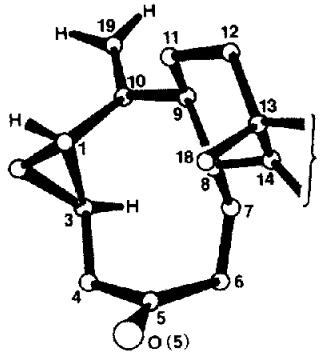
CD Spectra

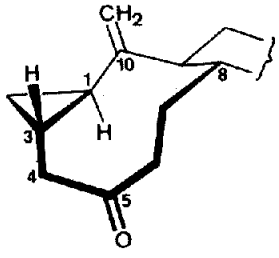
The CD maxima are summarized in Table 2. Compounds **3** and **4** contain each two chromophores which have well been investigated, *viz.* the saturated carbonyl and the vinyl cyclopropane. There are now many cases known where the preferred conformation in solution is very similar to that in the crystal, and so we shall too assume at first the same for the cyclononanone ring in ketones **3** and **4**, particularly since earlier ^{13}C-NMR measurements of these two compounds have also suggested such a similarity.[4a]†

An octant projection shows that the 9-membered ring has quite a different shape in ketones **3** and **4**, but the bulk of the other atoms is in a "negative" octant, and nevertheless, the CD is positive for both compounds. The two compounds **3** and **4** also differ in the geometrical

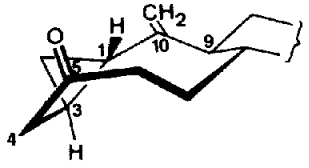
†Besides the arguments given there,[4a] we found, in addition, a pronounced upfield shift (6.6 ppm) for the signal of C(1) of **4** (δ 22.0 ppm) compared to that of **3** (δ 28.6 ppm); this can be assigned to the γ_{gauche} effect of C(11) which only in **4** has the proper geometry.





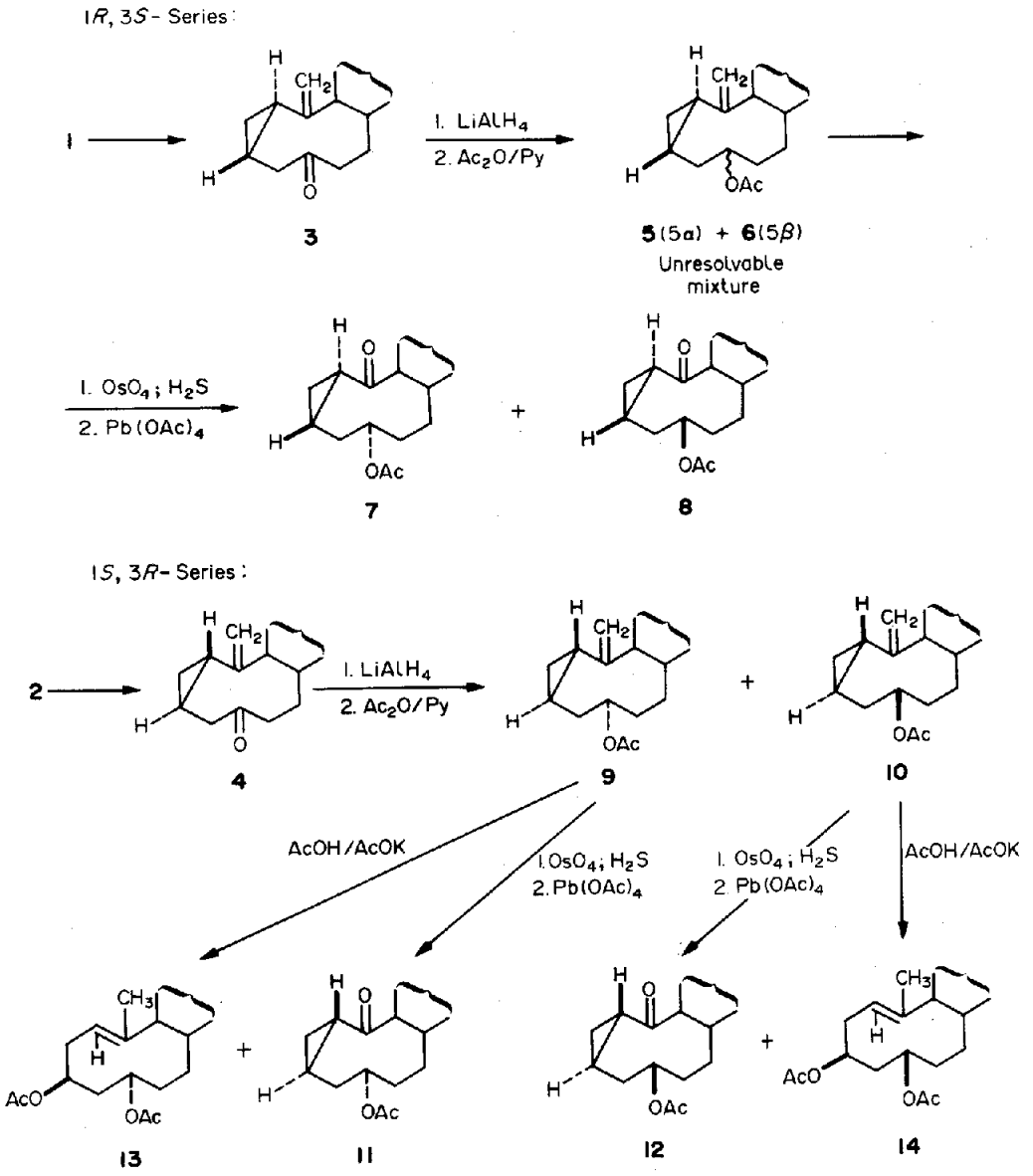


3-A



4-B

Scheme 2.



Scheme 3.

arrangement of the cyclopropane ring with respect to the C=O group, but the magnitudes of the Cotton effects are the same. On the other hand, the torsional angles around the C(4)–C(5) and C(5)–C(6) bonds are pairwise similar (−46.6° and −45° for the first, +86° and +60.5° for the second of these bonds) along the C–C–C–C train of bonds.[4b] Such values characterize a chiral second sphere around the chromophore,[8] and the signs of the contribution to the CD are opposite to the signs of these angles. A torsional angle of 0° clearly belongs to an achiral situation, and another such will be obtained at an angle somewhat smaller than 90°, because, since the coefficient for the MO-lobe between the two atoms of the perturbing σ-bond is greater than those of the outside lobes, at a torsional angle of 90° this σ-bond will already discriminate between the two possible orbital phase signs.[8] The signs so obtained are opposite to those for smaller torsional angles, so that the maximum CD-contribution is expected to appear at torsional angles of about 30–40°. This is in agreement with the general experience that the greatest CD-values are found for the C_2-twist cyclohexanone, where this torsional angle is around 30°. For ketones 3 and 4 the clntribution from that σ-bond asso-

Table 1. ^{1}H-NMR signals of H-C(5) in compounds 7, 8, 11 and 12[a]

Compound (and configuration)	Chem. shift δ (ppm)	Half-band width $w_{1/2}$ (Hz)	
7 (1R,3S-5α)	5.20	~12	(5β-H)
8 (1R,3S-5β)	4.78	~22	(5α-H)
11 (1S,3R-5α)	5.18	~17	(5β-H)
12 (1S,3R-5β)	4.78	~25	(5α-H)

[a] For further NMR data see Experimental.

Table 2. CD-Data for 1,3 - cyclo - 5,10 - seco - steroidal compounds 3–12 (in acetonitrile)[a]

Compound	λ_{max} ($\Delta\varepsilon$)
3	317(+0.75), 307(+1.22), 298(+1.22), 293sh(+1.03), 212(-6.1)
4	319(+0.67), 309(+1.23), 302(+1.32), 294(+1.11), 212sh(+8.5), 198(+11)
7	315sh(+0.07), 302sh(+0.17), 287(+0.28), 199(-1.3), positive at shorter wavelengths
8	319(+0.06), 306(+0.01), 278(+0.13), 201(-1.6), positive at shorter wavelengths
9	212(+5.2), stronger positive at shorter wavelengths
10	212(+5.2), stronger positive at shorter wavelengths
11	292(+2.72), 205(+0.8), negative at shorter wavelengths
12	288(+2.23), negative below 200 nm

[a] λ given in nm; "sh" indicates a shoulder

ciated with the negative torsional angle should thus dominate the Cotton effect, and the positive values found are in agreement with this expectation.

The correlation between the absolute conformation of a chiral vinyl cyclopropane moiety and its first CD-band around 210–220 nm has recently been discussed.[9] For a cisoid system the sign of the CD is the same as the sign of the torsional angle between the C=C bond and the bisectrix of the 3-membered cyclopropane ring. From X-ray diffraction data[4b] it was determined that this torsional angle is approximately − 30° for **3**, and + 34° for **4**. Consequently, in the 210–220 nm region a negative CD is expected for ketone **3**, a positive one for the diastereomer **4**, and this has indeed been found (Table 2). This good fit can thus be taken as a proof that the conformations of **3** (i.e. **A**) and **4** (i.e. **B**) in solution and in the crystal are indeed identical or, at least, very similar (Scheme 2).

The same vinyl cyclopropyl chromophore is also present in the epimeric 5-acetates **9** and **10** (both derived from ketone **4**), and molecular models suggest that the overall conformation of their nine-membered ring resembles that of **4**. In keeping with this, the CD of both these acetates around 210 nm is very close to that of ketone **4**.

In the 10-ketones **7**, **8**, **11** and **12** the carbonyl chromophore is "conjugated" with a cyclopropane ring, and such an arrangement gives a highly characteristic and usually strong Cotton effect for the n-π^* transition, if the 3-membered ring is in a transoid conformation to the C=O group;[10] for compounds with a cisoid conformation, however, too few examples exist and therefore no appropriate rule could be put forward.[10] An octant projection shows that the different atoms are distributed over positive and negative octants for **7** and **8** (derived from **3**), and this leads then—together with the not very pronounced contribution of a cisoid cyclopropane ring (with respect to the 10-keto group)—to the weak (positive) Cotton effect around 290 nm for these two compounds (i.e. **7** and **8**). Obviously, the cyclononanone ring has the same conformation in **7** and **8**, as is also born out by the nearly identical π–π^* band Cotton effects around 200 nm. On the other hand, the 5-epimeric 10-keto-5-acetates **11** and **12** (derived from **4**) give a medium strong positive CD for the n-π^* band, and this seems to reflect the distribution of most of the atoms into positive octants. For these two compounds (**11** and **12**) the CD π–π^* band is very weak, and in the CD-spectrum of **11** it has clearly the same sign (positive) as the one for the n-π^* transition. These two Cotton effects must, therefore, not always be of opposite signs, as claimed previously.[11] Although, thus, the CD of the 5-acetoxy-10-ketones **7**, **8**, **11** and **12** is not easily interpreted, it nevertheless can be quite useful for the comparison of conformations of related stereoisomers.

From the ^{1}H-NMR spectra one can infer, too, that epimerization at C(5) does not (appreciably) change the conformation of the cyclononanone ring: the half-band width of the H(5) signal is always larger for the 5β-acetoxy derivatives (**8** and **12**) than for the corresponding 5α-epimers (**7** and **11**, Table 1), indicating better antiperiplanar H/H arrangements for the two former compounds (i.e. **8** and **12**). Should the acetoxy grouping always prefer some equatorial orientation, then, for both 5β- and 5α-acetoxy epimers, similarly large (over 22 Hz) half-band width should be observed.

EXPERIMENTAL†

All m.ps are uncorrected. The CD spectra were recorded with a Jouan dichrograph model 185 at room temperature in acetonitrile, at concentrations of approximately 1 mg/ml. Optical rotations were measured in $CHCl_3$ soln. ^{1}H-NMR spectra were obtained at 100 MHz with a Varian HA-100 spectrometer in $CDCl_3$ soln at room temp, using TMS as internal standard; chemical shifts in ppm are reported as δ values (abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet). IR spectra were determined on a Perkin–Elmer double-beam instrument, model 337. Mass spectra were taken on an Atlas CH5 mass

†We wish to thank Dr. R. Tasovac (Microanalytical Laboratory, Faculty of Science, Belgrade) for carrying out elemental microanalyses. NMR spectral determinations were performed at Ciba-Geigy Ltd., Basle, Switzerland (direction Dr. H. Fuhrer), while IR and mass spectra were recorded at the Faculty of Science, Belgrade (direction Prof. D. Jeremić).

spectrometer. Silica gel (0.05–0.2 mm) was used for preparative column chromatography. The separation of products was monitored by tlc on silica gel G (Stahl) with benzene–AcOEt (9:1 or 7:3), detection being effected with 50% aqueous H_2SO_4. Light petroleum refers to the fraction b.p. 40–60°.

The preparation of the cyclopropane ring containing 5,10-seco - steroidal 5-ketones **3** and **4** was reported previously:[3] (1R,3S) - 1,3 - *cyclo* - 5,10 - *seco* - *cholest* - 10(19) - *en* - 5 - *one* (**3**), m.p. 154–155°, $[\alpha]_D^{20}+74°$ ($c=1.45$); (1S,3R) - 1,3 - *cyclo* - 5,10 - *seco* - *cholest* - 10(19) - *en* - 5 - *one* (**4**), m.p. 103°, $[\alpha]_D^{20}+58°$ ($c=0.54$).†

Transformations in the 1R,3S *series*

Reduction of the 5-ketone **3** *with lithium aluminium hydride and acetylation of the resulting epimeric 5-alcohols.* Ketone **3** (380 mg) was reduced with lithium aluminium hydride (150 mg) in dry diethyl ether (20 ml) at room temp for 10 min and the reaction mixture was worked up in the usual manner, to give the epimeric (1R,3S) - 1,3 - *cyclo* - 5,10 - *seco* - *cholest* - 10(19) - *en* - 5α- and -5β - *ols* (which appeared as one spot on TLC and were not separated). Upon treatment with Ac_2O (4 ml) in dry pyridine (4 ml), an unresolvable mixture of the corresponding 5α- and 5β-acetates **5** and **6** was obtained, which was used for subsequent transformations without further purification.

Hydroxylation of the mixture of the 5α- and 5β-acetates **5** *and* **6**, *and glycol cleavage of the resulting epimeric 5α, 10ξ, 19- and 5β, 10ξ, 19-triol 5-acetates.* To a solution of the **5+6** mixture (420 mg) in benzene (14 ml) and pyridine (12 ml), osmium tetroxide (300 mg) was added. The mixture was left at room temp for 72 h and then diluted with ethyl acetate (80 ml). H_2S was bubbled through the solution for 30 min and the insoluble salts were removed by filtration through a Celite mat. Evaporation of the solvents gave 450 mg (*ca.* 100%) of an unresolvable mixture of the epimeric (1R,3S) - 1,3 - *cyclo* - 5,10 - *seco* - *cholestane* - 5α, 10ξ, 19- and 5β, 10ξ, 19 - *triol* 5-*acetates*.

Lead tetraacetate (1.9 g) and these two diastereomers (450 mg) in dry benzene (45 ml) were stirred at room temp for 60 min. The resulting mixture was then diluted with wet diethyl ether, filtered through a Celite mat, and the insoluble precipitate washed with diethyl ether. The organic solution was washed with sat. $NaHCO_3$ aq and H_2O, dried over $MgSO_4$ and evaporated *in vacuo* to dryness, to give a mixture (390 mg, 92%), which was chromatographed on silica gel (40 g). Elution with benzene and benzene–diethyl ether (99:1) gave (1R,3S) - 5α - *acetoxy* - 19 - *nor* - 1,3 - *cyclo* - 5,10 - *seco* - *cholestan* - 10 - *one* **7** (125 mg, 29%), which was recrystallized from acetone–methanol (72 mg, 17%), m.p. 167°; $[\alpha]_D^{20}+36°$ ($c=0.5$); IR (KBr): ν_{max} 3040, 1740, 1702, 1250, 1238 cm^{-1}; NMR: δ 0.4–0.65 (2 cyclopropane H, m), 0.72 (Me-18, s), 0.86 (Me-26 and Me-27, d), 0.91 (Me-21, d), 2.00 (AcO-5α, s), 5.20 (H-5β, m, half-band width ~12 Hz). (Found: C, 78.29; H, 10.94. Calc. for $C_{28}H_{46}O_3$: C, 78.09; H, 10.77%).

Further benzene–diethyl ether (99:1) eluates afforded (1R,3S) - 5β - *acetoxy* - 19 - *nor* - 1,3 - *cyclo* - 5,10 - *seco* - *cholestan* - 10 - *one* **8** (180 mg, 42%), which was recrystallized from acetone–methanol (110 mg, 26%), m.p. 127°; $[\alpha]_D^{20}+44°$ ($c=0.5$); IR (KBr): ν_{max} 3020, 1735, 1700, 1242 cm^{-1}; NMR: δ 0.5–0.65 (2 cyclopropane H, m), 0.70 (Me-18, s), 0.86 (Me-26 and Me-27, d), 0.91 (Me-21, d), 1.99 (AcO-5β, s), 4.78 (H-5α, m, half-band width ~22 Hz). (Found: C, 78.22; H, 11.01. Calc. for $C_{28}H_{46}O_3$: C, 78.09; H, 10.77%).

Transformations in the 1S,3R-*series*

Reduction of the 5-ketone **4** *with lithium aluminium hydride and acetylation of the resulting epimeric 5-alcohols.* Ketone **4** (730 mg) was reduced with lithium aluminium hydride (140 mg) in dry diethyl ether (20 ml) under reflux, and then, after the usual work-up, the resulting epimeric 5-alcohols were acetylated as described above, and the residue was chromatographed on silica gel (30 g). Light petroleum-benzene (8:2) (200 ml) eluted 278 mg (34%) of (1S,3R) - 1,3 - *cyclo* - 5,10 - *seco* - *cholest* - 10(19) - *en* - 5α - *ol acetate* **9**, which was recrystallized from acetone (260 mg, 32%), m.p. 104°; $[\alpha]_D^{20}+38°$ ($c=0.46$); IR (KBr): ν_{max} 3080, 3025, 1730, 1640, 1248 cm^{-1}; NMR: δ 0.4–0.65 (2 cyclopropane H, m), 0.78 (Me-18, s), 0.87 (Me-26 and Me-27, d), 0.90 (Me-21, d), 2.00 (AcO-5α, s), 4.46 and 4.55 (2 exocyclic vinyl H at C-19), 5.24 (H-5β, m). (Found: C, 81.36; H, 11.36. Calc. for $C_{29}H_{48}O_2$: C, 81.25; 11.29%).[7]

Elution with light petroleum–benzene (6:4) (100 ml) gave 270 mg (33%) of (1S,3R) - 1,3 - *cyclo* - 5,10 - *seco* - *cholest* - 10(19) - *en* - 5β - *ol acetate* **10**, as an oil; MS: *m/e* 428 (M^+); $[\alpha]_D^{20}+23°$ ($c=1.95$); IR (CCl_4); ν_{max} 3070, 3010, 1730, 1635, 1238 cm^{-1}; NMR: δ 0.4–0.6 (2 cyclopropane H, m), 0.72 (Me-18, s), 0.86 (Me-26 and Me-27, d), 0.91 (Me-21, d), 1.97 (AcO-5β, s), 4.45 and 4.54 (2 exocyclic vinyl H at C-19), 4.82 (H-5α, m).[7]

Hydroxylation of the 5α-acetate **9** *and glycol cleavage of the resulting 5α, 10ξ, 19-triol 5-acetate.* Compound **9** (260 mg) was hydroxylated with osmium tetroxide (185 mg) in benzene (8 ml) and pyridine (7 ml) soln at room temp for 32 h. The mixture was then treated with H_2S (as described above) to give 280 mg (~100%) of (1S,3R) - 1,3 - *cyclo* - 5,10 - *seco* - *cholestane* - 5α,10ξ,19-*triol* 5-*acetate*, which, without further purification, was oxidized with lead tetraacetate (1.2 g) in dry benzene (30 ml), as described above. The product obtained was dissolved in benzene, passed through an Al_2O_3 column, and the filtrate evaporated *in vacuo* to dryness. The residue was recrystallized from methanol to give 135 mg (52%) of (1S,3R) - 5α - *acetoxy* - 19 - *nor* - 1,3 - *cyclo* - 5,10 - *seco* - *cholestan* - 10 - *one* **11**, m.p. 123–124°; $[\alpha]_D^{20}+19°$ ($c=0.2$); IR (KBr): ν_{max} 3085, 3010, 1740, 1695, 1235 cm^{-1}; NMR: δ 0.50–0.75 (2 cyclopropane H, m), 0.82 (Me-18, s), 0.88 (Me-26 and Me-27, d), 0.93 (Me-21, d), 2.02 (AcO-5α, s), 5.18 (H-5β, m, half-band width ~17 Hz). (Found: C, 77.93; H, 10.65. Calc. for $C_{28}H_{46}O_3$: C, 78.09; H, 10.77%).

Hydroxylation of the 5β-acetate **10** *and glycol cleavage of the resulting 5β,10ξ,19-triol 5-acetate* Compound **10** (110 mg) was hydroxylated with osmium tetroxide (80 mg) in benzene (3.5 ml) and pyridine (3 ml) for 30 h (at room temp). Treatment with H_2S as above afforded 120 mg (~100%) of (1S,3R)-1,3 - *cyclo* - 5,10 - *seco* - *cholestane* - 5β,10ξ,19 - *triol* 5-*acetate*, which, without further purification, was oxidized with lead tetraacetate (600 mg) in dry benzene (16 ml), as described above. The product, dissolved in benzene, was passed through a short Al_2O_3 column, and the filtrate evaporeated *in vacuo* to dryness. Crystallization of the residue (about 100 mg) from acetone–methanol afforded 64 mg (62%) of (1S,3R) - 5β - *acetoxy* - 19 - *nor* - 1,3 - *cyclo* - 5,10 - *seco* - *cholestan* - 10 - *one* **12**, m.p. 135°; IR (KBr): ν_{max} 3035, 3010, 1745, 1700, 1245 cm^{-1}; NMR: δ 0.5–0.7 (2 cyclopropane H, m), 0.76 (Me-18, s), 0.86 (Me-26 and Me-27, d), 0.91 (Me-21, d), 1.98 (AcO-5β, *s*), 4.78 (H-5α, m, half-band width ~25 Hz). (Found: C, 78.18; H, 11.04. Calc. for $C_{28}H_{46}O_3$: C, 78.09; H, 10.77%).

Acetolysis of (1S,3R) - 1,3 - *cyclo* - 5,10 - *seco* - *cholest* - 10(19) - *en* - 5α - *ol acetate* **9**. To a soln of 5α-acetate **9** (200 mg) in glacial AcOH (16 ml), anhydrous potassium acetate (56 mg) was added and the mixture heated at 50° for 24 h. It was then diluted with water, extracted with diethyl ether, the ethereal layer neutralized with sat. $NaHCO_3$ aq and H_2O, dried over $MgSO_4$ and evaporated *in vacuo* to dryness, to give 196 mg (86%) of (E) - 5,10 - *seco* - *cholest* - 1(10) - *ene* - 3β,5α - *diol diacetate* **13**, which was recrystallized from acetone–methanol (174 mg, 77%), m.p. 95–96° (undepressed by admixture of an authentic sample[6]).

Acetolysis of (1S,3R) - 1,3 - *cyclo* - 5,10 - *seco* - *cholest* - 10(19) - *en* - 5β - *ol acetate* **10**. Compound **10** (200 mg) was treated with glacial AcOH (16 ml) and anhydrous potassium acetate (56 mg) as above, to give 201 mg (88%) of (E) - 5,10 - *seco* - *cholest* - 1(10) - *ene* - 3,5 - *diol diacetate* **14**, which was recrystallized from acetone–methanol (180 mg, 79%), m.p. 104–105° (undepressed by admixture of an authentic sample[7]).

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†The ^1H- and ^{13}C-NMR spectra of ketones **3** and **4** were discussed in our earlier papers.[3,4a]

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