Pentacyclic Steroids. Part 1. Synthesis and *X*-Ray Conformational Analysis of 4α,5β- and 4α,5α-Dihydrobenzo[4,5,6]cholestan-5'(6'*H*)-one

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Conjugate alkylation of cholest-4-en-6-one (1) with the homocuprate derived from the reaction of lithiated acetone *NN*-dimethylhydrazone with copper(I) iodide, followed by acidic hydrolysis, afforded 4β-(2-oxopropyl)-5α- and -5β-cholestan-6-one (3) and (4). The latter compound underwent intramolecular aldol condensation, and the derived hydroxy ketone was converted into 4α,5β- and 4α,5α-dihydrobenzo[4,5,6]cholest-4-en-5'(6'*H*)-one (9) and (10), the structures and conformations of which were investigated by *X*-ray crystallography.

Although a number of syntheses of benzo[4,5,6]steroids have been reported,[1] little attention has been given to compounds in which the additional ring is partially or fully saturated. Eight stereoisomeric '4,6-propanocholestanes' can be generated through configurational changes at C(4), C(5), and C(6), some of which would be subject to constraints necessitating the adoption of abnormal ring conformations. Rings A, B, and E of these substances represent conformationally rigid models of the rare perhydrophenalene ring system.[2]

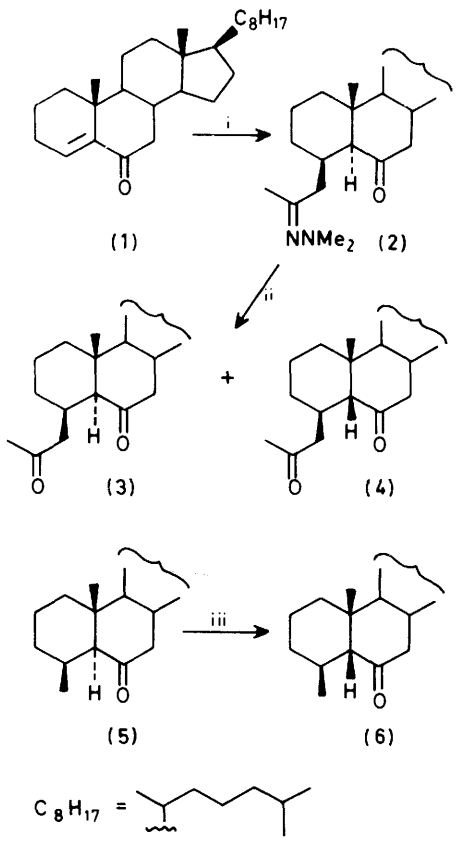
An investigation of stereocontrolled syntheses of '4,6-propanocholestanes' was undertaken in order to study their interconversions and conformational properties. For these purposes it was considered desirable to incorporate functionality on ring E, and a suitable approach was envisaged through conjugate addition of a functionalised C_3-synthon to cholest-4-en-6-one (1), followed by closure between C(6) and the chain terminus.

Treatment of (1) with the homocuprate derived from the reaction of lithiated acetone *N,N*-dimethylhydrazone with copper(I) iodide in the presence of di-isopropyl sulphide [3] afforded the desired product (2), which underwent partial decomposition during chromatography on silica gel. Nevertheless, a recrystallised sample of (2), obtained from the more polar column fractions, displayed the expected properties. In practice, it was advantageous to first hydrolyse the primary alkylation product with ethanolic hydrochloric acid; chromatography of the resultant product afforded 4β-(2-oxopropyl)-5α-cholestan-6-one (3) (50%) and the corresponding 5β-cholestane isomer (4) (15%). The assignment of 4β-configuration to both of these products is based upon analogy,[4,5] and was confirmed by subsequent transformations.

The 5α- and 5β-isomer (3) and (4) were readily distinguished by their spectroscopic properties (see later) and by comparison with 4β-methyl-5α- and 4β-methyl-5β-cholestan-6-one (5) and (6); the latter product was prepared by base-catalysed isomerisation of (5), as described [4] for a related compound.

Although the equilibration of (3) and (4) could not be examined, owing to the intervention of intramolecular aldol condensation, it may be assumed that the 5β-isomer (4) is thermodynamically favoured, in view of the ease of formation of (6) from (5). It seems likely that partial equilibration at C(5) must take place during hydrolysis of the hydrazone (2), since the work-up conditions of the conjugate-alkylation product were sufficiently mild to ensure kinetically controlled protonation of the 5-en-6-olate anion, whereas the prolonged exposure to acid during the next step would favour a degree of equilibration.

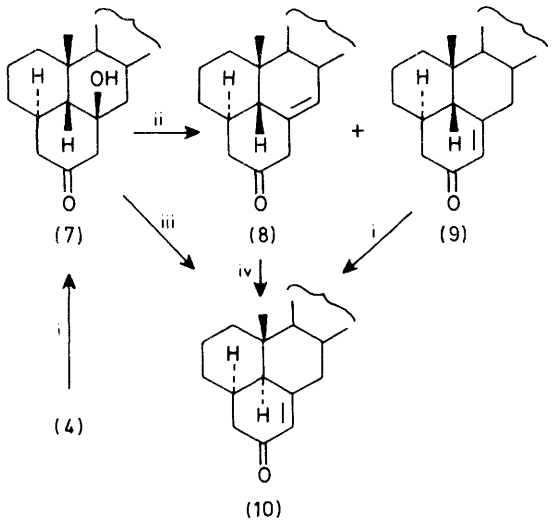
Treatment of (3) or (4) with ethanolic 0.4M-potassium hydroxide at 25 °C afforded a single β-hydroxy ketone (7). T.l.c. monitoring of the progress of these reactions revealed



Reagents: i, $[MeC(=NNMe_2)CH_2]_2CuLi$, THF; ii, HCl, EtOH; iii, KOH, MeOH, heat

that the 5β-isomer (4) was converted rapidly and directly into the product (7), whereas the reaction of the 5α-isomer (3) proceeded more slowly, and through the intermediacy of (4). It was therefore concluded that the cyclisation product was a 5β-isomer, and consequently, that condensation had occurred on the α-face, to give the 6β-hydroxy-5'-ketone (7).

Examination of models provided a reasonable explanation for the absence of competing intramolecular aldol condensation to give a 6α-hydroxy-5α-isomer. Whereas the alignment of groups in the 5β-isomer (4) leads easily and stereospecifically to the product (7), the adoption of a favourable 4β-side-chain conformation for closure in the 5α-isomer (3) would be severely impeded by steric interactions with the 10β-methyl group (Figure 1).



Reagents: i, KOH, EtOH, 25 °C; ii, $SOCl_2$, C_5H_5N, 20 °C; iii, KOH, EtOH, heat; iv, *p*-TsOH, C_6H_6, heat

Attention was turned to the preparation of a useful synthetic intermediate in the 5α-series. Thus, the hydroxy ketone (7) underwent β-elimination and isomerisation upon treatment with refluxing ethanolic 0.4M-potassium hydroxide to give the 5α-$\Delta^{6(4')}$-5′-ketone (10). Although the progress of this reaction was monitored continuously (t.l.c.), no intermediate 5β-isomer (9) could be detected. In a separate experiment, the 5β-compound (9) was readily isomerised to (10) in the presence of alkali. Furthermore, treatment of the 5β-Δ^6-5′-ketone (8) with toluene-*p*-sulphonic acid in refluxing benzene also led to the 5α-$\Delta^{6(4')}$-5′-ketone (10). These results clearly demonstrate that the 5α-product is thermodynamically favoured; this is further borne out by an examination of models, which reveals that ring B of the 5β-$\Delta^{6(4')}$-5′-ketone (9) is constrained to adopt a boat-like conformation, whereas the 5α-isomer (10) can be accommodated in an all-chair structure, albeit one in which rings A and E appear to be rather strained. Interestingly, the Δ^6-compound (8) does not appear to be subject to any unusual conformational features, possibly because the Δ^6-bond is compatible with torsional strain minimisation in an A,B-*cis*-skeleton.[6]

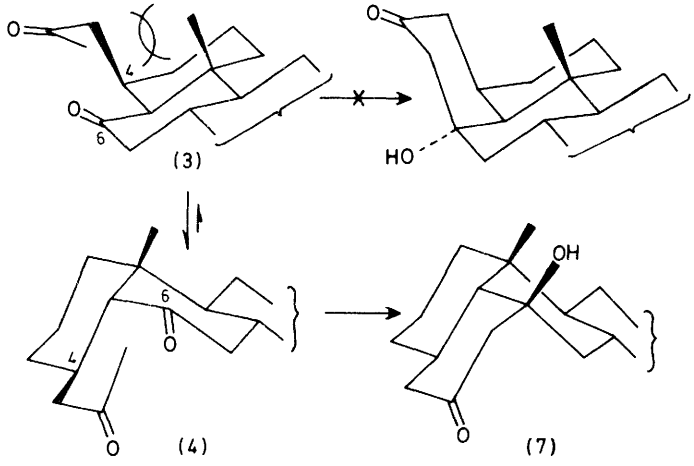


Figure 1. Selective aldol closure of the 5β-2′,6-diketone (4)

Preliminary experiments showed that alkali-mediated β-elimination of the hydroxy ketone (7) resulted in concomitant inversion at C(5) (see later), and accordingly, alternative methods were sought for converting (7) into useful intermediates for further elaboration of the 5β-series. It was reasoned that kinetically controlled dehydration of (7) would result in favoured antiperiplanar elimination toward C(7). Indeed, treatment of (7) with thionyl chloride in pyridine at 0 °C gave a major product (65%), the properties of which were consistent with the expected structure (8). It was accompanied by the 5β-$\Delta^{6(4')}$-5′-ketone (9) (17%), but no products attributable to synperiplanar elimination toward C(5), or to skeletal rearrangement, were detected.

The β,γ-unsaturated ketone (8) was extremely labile, and underwent partial decomposition in solution and during chromatography. Furthermore, it failed to isomerise to the α,β-unsaturated ketone (9) upon alkaline treatment. This implies that the 4′,6-dien-5′-olate anion resists protonation at C(7). Attempted catalytic hydrogenation of the Δ^6-compound (8) also failed; models show that the α and β faces of the olefinic bond are severely hindered. These results militate against further elaboration of the 5β-series of pentacyclic compounds by this route.

Structural Assignments.—The structures of the compounds (2)—(10) were confirmed by spectroscopy; ^{13}C n.m.r. (Table 1) and c.d. (Table 2) data were particularly helpful in differentiating 5α- and 5β-isomers, and in identifying unusual conformational features. ^{13}C Assignments were made upon PND* and SFORD* spectra and, in some instances, with the additional aid of gated spin echo (GASPE) experiments [7] for distinguishing carbon atoms attached to an odd or even number of hydrogen atoms.

The C(5) configurations of the compounds (2)—(10) were readily determined by the chemical shifts of the C(9) and C(19) resonances.[8] The 4β-alkyl-5α-isomers (2), (3), and (5) displayed C(9) chemical shifts very similar to that of 5α-cholestane, and a consistent downfield shift of C(19) (*ca.* 4 p.p.m.), ascribed to the combined influence of the 6-oxo group (*ca.* 1 p.p.m.) and the *syn*-diaxial [9] interaction (*ca.* 3 p.p.m.) with the 4β-alkyl group. The C(9) and C(19) resonances of the 4β-alkyl-5β-isomers (4) and (6) were very similar to those of 5β-cholestan-6-one. The expected α-, β-, and γ-effects of 4β-alkyl substitution were present in (2)—(6), and it is

* PND = proton noise-decoupled. SFORD = single-frequency off-resonance decoupled.

Table 1. ^{13}C N.m.r. data of compounds (2)—(10) [a]

Compd.	Carbon atom 1	2	3	4	5	6	7	8	9	10	19	Other
5α-Compounds												
(2)	38.4	17.0	29.7	28.0	61.7	211.6	47.0	36.3	54.9	40.6	16.1	47.0 (1′), 168.8 (2′), 28.0 (3′)
(3)	38.3	17.1	30.2	27.5	60.6	211.7	47.2	36.8	55.0	41.0	16.1	44.3 (1′), 208.7 (2′), 30.0 (3′)
(5)	38.7	17.1	33.0	27.3	61.6	*b*	47.2	36.4	55.2	40.8	16.2	16.6 (1′)
5β-Compounds												
(4)	36.1	20.2	32.6	31.2	66.8	215.1	39.7	37.5	39.5	43.1	23.9	48.7 (1′), 207.4 (2′), 30.6 (3′)
(6)	36.2	20.7	34.8	31.1	68.8	215.0	39.9	38.0	41.3	43.3	23.9	20.0 (1′)
Cyclised compounds												
(7)	35.3	20.6	39.5	32.7	57.8	76.7	38.9	34.6	41.5	37.0	27.4	58.4 (4′), 49.0 (6′)
(8)	37.3	20.7	39.4	34.2	53.0	134.5	123.6	36.6	41.0	34.4	23.9	53.3 (4′), 207.8 (5′), 49.6 (6′)
(9)	34.5	17.9	34.5	35.1	51.4	169.5	29.7	34.3	46.8	36.4	23.4	127.2 (4′), 199.3 (5′), 45.8 (6′)
(10)	37.1	17.6	29.8	31.9	50.4	167.0	41.6	39.5	56.2	41.2	15.4	123.6 (4′), 201.0 (5′), 39.6 (6′)

[a] Recorded on a Varian CFT-20 instrument for deuteriochloroform solutions using tetramethylsilane as internal standard. Chemical shifts of C(11)—C(18) and C(20)—C(27) usually showed close correspondence to those recorded for 5α- or 5β-cholestane and are omitted; exceptions are discussed in the text. [b] Not recorded.

Table 2. C.d. data for compounds (2)—(10) [a]

Compound	$\lambda_{max.}$/nm	Δε
4β-[$CH_2C(=NNMe_2)Me$]-5α-6-one (2)	306	−0.6 [b]
	264	3.1
4β-(CH_2COMe)-5α-6-one (3)	292	−2.0
4β-(CH_2COMe)-5β-6-one (4)	297	−4.6
4β-Me-5α-6-one (5)	298	−0.9 [c]
4β-Me-5β-6-one (6)	294	−4.4
6β-OH-5β-5′-one (7)	283	−0.2
Δ^6-5β-5′-one (8)	296	2.8
$\Delta^{6(4')}$-5β-5′-one (9)	319	2.0
	248	−4.2
$\Delta^{6(4')}$-5α-5′-one (10)	322	1.8
	238	8.8

[a] Recorded on a Jasco J-20 instrument for methanol solutions. [b] Apparent maximum in bisignate curve. [c] Previously reported [5] value of −1.65 is incorrect.

noteworthy that C(3) in the 4β-oxopropyl-5α-derivatives (2) and (3) experiences a significant shielding effect (*ca.* −3 p.p.m.), suggestive of a *gauche* relationship with the C(1′)–C(2′) bond. A related but smaller effect is present in the 5β-isomer (4).

The trends observed for the c.d. spectra of (3) and (4) were similar to those of 5α- and 5β-cholestan-6-one respectively. However, comparisons with 4β-methyl-5α-cholestan-6-one (5) and its corresponding 5β-isomer (6) were more meaningful. Thus, it is evident that the 4β-alkyl groups in the 5β-compounds (4) and (6) make a negligible contribution to their chiroptical behaviour, since the Cotton effects show close mutual correspondence and are very similar to that reported [10] for 5β-cholestan-6-one ($\Delta\varepsilon_{294}$ − 4.2 in methanol). However, the 4β-methyl group of (5) is responsible for a positive increment (ΔΔε 0.7) relative to 5α-cholestan-6-one [10] ($\Delta\varepsilon_{292}$ − 1.6 in methanol), whereas the 4β-(2′-oxopropyl) group in (3) gives rise to a negative increment (ΔΔε − 0.4). This discrepancy may reflect mutual perturbation of the 6- and 2′-oxo groups in (3), but an alternative or contributory factor may be the net Cotton effect of the latter chromophore. Thus, if it is assumed that the 4β-side-chain in (3) is constrained to adopt that *gauche* conformation in which the C(1′)–C(2′) bond lies between C(4)–C(3) and C(4)–H(4α), in order to minimise interactions with the elements of ring A, the 2′-oxo-group would be expected to give rise to a negative Cotton effect. The magnitude of this effect cannot be predicted, but it would contribute toward the observed discrepancy (ΔΔε − 1.1) between (5) and (3). The bisignate nature of the c.d. spectrum of the related 2′-hydrazone (2) obscured the contribution of the 6-oxo group, but the apparent value of $\Delta\varepsilon_{306}$, 0.6, is close enough to that of the 4β-methyl compound (5) to support the proposal. Furthermore, the suggested conformation of the 4β-side-chain in (2) and (3) provides an explanation for the γ-*gauche* shielding of C(3) (see above).

The ^{13}C chemical shifts of C(9) and C(19) in the cyclised compounds (7)—(10) confirmed the assignments for the 5-configuration.[8] In the case of the primary cyclisation product (7), the further downfield shift (*ca.* 4 p.p.m.) of the C(19) resonance was ascribed to the *syn*-diaxial [9] disposition of the 6β-hydroxy group. It is significant that the C(9) resonance of the 5β-$\Delta^{6(4')}$-5′-ketone (9) was deshielded by comparison with the other 5β-isomers discussed here, and that some of the other ring-A and -B carbon atoms displayed chemical shifts which were anomalous in terms of simple substitution effects.[11] Furthermore, the chemical shifts of C(11) (22.1 p.p.m.) and C(14) (55.5 p.p.m.) deviated sufficiently from those measured for 5β-cholestane [11] to confirm that ring deformations were responsible. However, it was not possible to identify the nature of such deformations using these data.

Although the c.d. data for the conjugated enones (9) and (10) are not in conflict with the structural assignments, it is necessary to assume that the chromophore is coplanar in both cases and that the similar magnitudes of the positive Cotton effects for the $n \longrightarrow \pi^*$ transition are determined by the residual ring helicity.[12] The opposing signs of the $\pi \longrightarrow \pi^*$ Cotton effects in (9) and (10) may then be ascribed to the influence of the pseudo-axial allylic bonds in ring B. These conclusions are not obvious from an examination of models, nor do the c.d. data provide direct evidence for the suspected ring deformation in the 5β-compound (9).

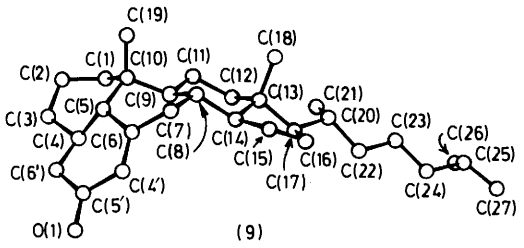
In order to obtain further insight into the conformational properties of these substances, the structures of compounds (9) and (10) were determined by *X*-ray crystallography.

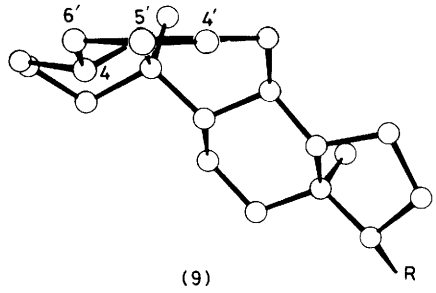
X-Ray Crystallography.—Details of the *X*-ray crystallographic analysis of the α,β-unsaturated ketones (9) and (10) are given in the Experimental section, and the structures are depicted in Figure 2.

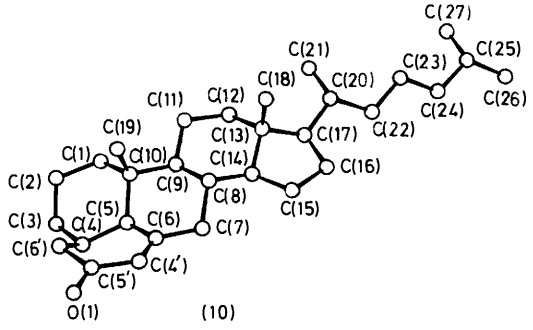
The method of Cremer and Pople [13] was used to calculate the puckering parameters of the rings in (9) and (10), and their conformations are described with the aid of defined [14] nomen-

Table 3. Puckering parameters for compounds (9) and (10)

	θ (°)		φ (°)		Q/Å		Conformation	
Ring	(9)	(10)	(9)	(10)	(9)	(10)	(9)	(10)
A	91.1	172.3	160.8	140.8	0.75	0.51	$^5T_1 + B_{4,1}$ (2 : 1)	$^2H_1 + {}^4C_1$ (1 : 4)
B	97.6	165.6	275.1	219.8	0.71	0.58	$^{10}T_6$	$^{10}H_5 + {}^8C_5$ (2 : 1)
C	5.4	1.8	342.1	6.3	0.60	0.58	$^8C_{12}$	$^8C_{12}$
D	—	—	346.2	351.0	0.47	0.46	$^{13}E + {}^{13}_{14}T$ (1 : 4)	$^{13}E + {}^{13}_{14}T$ (1 : 1)
E	124.7	125.4	179.6	166.9	0.46	0.44	E_4	$^{6'}H_4 + E_4$ (1 : 1)







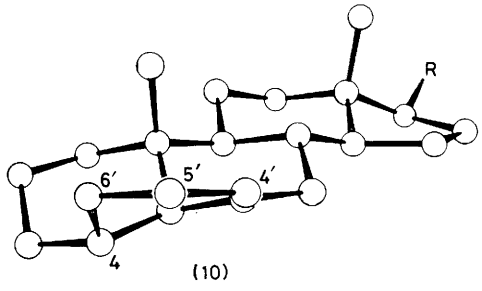


Figure 2. *X*-Ray structures of (9) and (10), with the atomic numbering scheme shown

Figure 3. Projections along O(1)–C(5′) of (9) and (10), generated from *X*-ray data

clature (Table 3). These data demonstrate the substantial differences in conformational properties of the two compounds.

Thus, ring A of the 5α-compound (10) displays a minor component of half-chair character, whereas ring B is more strongly distorted toward a half-chair conformation. Both of these deviations from the respective chair conformations ($^4C_1$ and $^8C_5$) can be ascribed to flattening imposed by ring E, whereby steric interactions with the 10β-methyl group are relieved. However, the overall effect of the additional ring in (10) is unexceptional.

By contrast, both rings A and B of the 5β-compound (9) suffer substantial deformation, the former to a hybrid twist-boat, and the latter to a twist conformation. As expected, both rings are strongly puckered. This is a further [15] example of the rare phenomenon of steroids having two contiguous boat-like rings, and provides an explanation for the anomalous chemical shifts of the ^{13}C-resonances. The conformation of (9) is of particular interest, since models reveal that, whereas ring B is constrained to adopt a boat-like conformation, the only advantage of attendant deformation of ring A from a $^1C_4$ form is minor relief of steric interactions on the α-face of the molecule. Therefore, it is inferred that the energy barrier to interconversion between $^1C_4$ and $^5T_1 + B_{4,1}$ forms must be sufficiently lowered by the *cis*-fusion of rings A and B to make this factor decisive.

A comparison of the crystallographically determined conformations of ring E in (9) and (10) reveals that the former approximates closely to an envelope, whereas the latter displays hybrid envelope–half-chair character. In both cases the elements of the chromophore [C(6)–C(4′)–C(5′)–O] are sufficiently close to coplanarity to support the foregoing conclusion, such that the similar magnitudes of their positive $n \longrightarrow \pi^*$ Cotton effects are solely attributable to the influence of the C(6′)–C(4) bond. Accordingly the signs of the $\pi \longrightarrow \pi^*$ Cotton effects are determined by the first chiral elements of ring B. These features are illustrated in Figure 3.

The conformations of rings C and D in (9) and (10) are unexceptional (Table 3).

Experimental

M.p.s were determined on a Kofler hot-stage apparatus. Unless otherwise specified, spectra were recorded as follows: i.r., Perkin-Elmer 257, chloroform solutions; u.v., Unicam SP8-100, ethanol solutions; ^{1}H n.m.r., Varian EM-390,

deuteriochloroform solutions with tetramethylsilane as internal standard; ^{13}C n.m.r., Varian CFT-20, deuteriochloroform solutions with tetramethylsilane as internal standard; mass (electron impact), Varian MAT 212; c.d., Jasco J-20, methanol solutions. Optical rotations were measured in chloroform solutions at 24 °C, on a Perkin-Elmer 241 polarimeter. Silica gel for column chromatography refers to Merck Kieselgel 60, and h.p.l.c. was carried out on a Waters PrepLC System 500 using PrepPAK 500 silica gel cartridges.

4β-(2′-*Oxopropyl*)-5α-*cholestan*-6-*one* 2′-*Dimethylhydrazone* (2).—n-Butyl-lithium (1.6M; 8 ml) was added to acetone *N*,*N*-dimethylhydrazone (1.3 g) in dry tetrahydrofuran (THF) (15 ml) at −78 °C under nitrogen. After 20 min, a precooled (*ca.* −30 °C) solution of copper(I) iodide (1.3 g) and di-isopropyl sulphide (3.1 g) in dry THF (15 ml) was added dropwise at −78 °C. The reaction mixture was allowed to warm up to 0 °C during 40 min, then it was recooled to −78 °C, and a solution of cholest-4-en-6-one (1) (0.5 g) in dry THF (20 ml) was added dropwise. After 2 h at −78 °C the mixture was allowed to warm up to room temperature overnight, and was quenched with aqueous ammonium chloride–ammonium hydroxide (pH 8). The mixture was extracted with benzene, and the organic phase was washed repeatedly with aqueous ammonium chloride–ammonium hydroxide until the aqueous phase remained colourless. The extract was dried over anhydrous magnesium sulphate and evaporated under reduced pressure. Chromatography of the residue on silica gel (75 g) with ethyl acetate–benzene (1 : 9) gave the 5α-2′,6-diketone (3) (0.18 g) (see following experiment) followed by the 2′-dimethylhydrazone (2) (0.2 g), m.p. 150—155 °C (from acetone); $[\alpha]_D$ +36° (*c* 1.3); $\nu_{max.}$ 1 695 (CO) and 1 600 cm^{-1} (C=N); δ 0.66 (3 H, s, 13-Me), 0.83 (3 H, s, 10-Me), 2.08 (3 H, s, 3′-H_3), and 2.43 (6 H, s, $NNMe_2$) (Found: M^+, 484.437. $C_{32}H_{56}N_2O$ requires *M*, 484.439).

Hydrolysis of the 2′-*Dimethylhydrazone* (2).—The crude 2′-dimethylhydrazone (2), prepared from cholest-4-en-6-one (1) (5 g) as described in the foregoing experiment, was treated with 1.5M-hydrochloric acid (14 ml) in ethanol (50 ml) at 25 °C for 24 h. Aqueous sodium hydrogen carbonate was added and the mixture was extracted with benzene to give material (3.98 g) which was shown by multiple-development t.l.c. to comprise two components, but which failed to separate on column chromatography. Preparative h.p.l.c. with ethyl acetate–benzene (1 : 9) afforded 4β-(2′-*oxopropyl*)-5α-*cholestan*-6-*one* (3) (2.85 g), m.p. 104—106 °C (from acetone); $[\alpha]_D$ +33° (*c* 1.1); $\nu_{max.}$ 1 714sh and 1 692 cm^{-1} (CO); δ 0.66 (3 H, s, 13-Me), 0.81 (3 H, s, 10-Me), and 2.19 (3 H, s, COMe) (Found: C, 81.2; H, 11.6%; M^+, 442. $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.4%; *M*, 442), followed by mixed fractions (0.295 g) and 4β-(2′-*oxopropyl*)-5β-*cholestan*-6-*one* (4) (0.841 g), m.p. 82—84 °C (from acetone); $[\alpha]_D$ − 41° (*c* 1.0); $\nu_{max.}$ 1 715sh and 1 690 cm^{-1} (CO); δ 0.64 (3 H, s, 13-Me), 0.8 (3 H, s, 10-Me), and 2.07 (3 H, s, COMe) (Found: C, 81.5; H, 11.55%; M^+, 442).

4β-*Methyl*-5β-*cholestan*-6-*one* (6).—4β-Methyl-5α-cholestan-6-one (5) (0.4 g) in methanolic 0.2M-potassium hydroxide (45 ml) was refluxed under nitrogen for 5 h. The mixture was acidified and diluted with water, and the product was isolated by extraction with benzene and purified by filtration through silica gel (10 g) with ethyl acetate–benzene (3 : 97) to give the 5β-*isomer* (6) (0.39 g), m.p. 110—112 °C (from acetone); $[\alpha]_D$ −50° (*c* 1.0); $\nu_{max.}$ 1 690 cm^{-1} (CO); δ 0.66 (3 H, s, 13-Me) and 0.83 (3 H, s, 10-Me) (Found: C, 84.1; H, 12.2%; M^+, 400. $C_{28}H_{48}O$ requires C, 84.0; H, 12.1%; *M*, 400).

6-*Hydroxy*-4α,4′,5β,6β-*tetrahydrobenzo*[4,5,6]*cholest*-4-*en*-5′(6′H)-*one* (7).—(a) The 5α-2′,6-diketone (3) (0.134 g) was treated with ethanolic 0.4M-potassium hydroxide at 25 °C under nitrogen for 48 h. Solid CO_2 was added and the product was isolated by extraction with benzene, and chromatographed on silica gel (10 g) with ethyl acetate–benzene (1 : 9) to give the *hydroxy ketone* (7) (0.106 g), m.p. 145—147 °C (from hexane); $[\alpha]_D$ −4° (*c* 1.1); $\nu_{max.}$ 3 680 (OH) and 1 710 cm^{-1} (CO); δ 0.69 (3 H, s, 13-Me) and 1.2 (3 H, s, 10-Me) (Found: C, 81.5; H, 11.4%; M^+, 442. $C_{30}H_{50}O_2$ requires C, 81.4; H, 11.4%; *M*, 442).

(b) Similar treatment of the 5β-2′,6-diketone (4) (0.143 g) for 24 h, followed by chromatography, afforded the identical product (7) (0.14 g).

Dehydration of the Hydroxy Ketone (7) *with Thiony Chloride–Pyridine*.—Thionyl chloride (0.025 ml) in pyridine (0.05 ml) was added dropwise to a solution of the hydroxy ketone (7) (0.1 g) in pyridine (0.2 ml) at 20 °C. After 1 h, the mixture was poured into water and the product was isolated by extraction with benzene. Preparative h.p.l.c. with ethyl acetate–hexane (1 : 9) afforded 4α,4′,5β,6-tetrahydrobenzo-[4,5,6]cholesta-4,6-dien-5′(6′*H*)-one (8) (0.062 g) as an oil, $[\alpha]_D$ +41° (*c* 0.7); $\nu_{max.}$ 1 700 cm^{-1} (CO); δ 0.67 (3 H, s, 13-Me), 0.92 (3 H, s, 10-Me), 3.0 (2 H, s), and 5.26 (1 H, br, $w_{\frac{1}{2}}$ 4 Hz, 7-H) (Found: M^+, 424.366. $C_{30}H_{48}O$ requires *M*, 424.370), followed by 4α,5β-*dihydrobenzo*[4,5,6]*cholest*-4-*en*-5′(6′H)-*one* (9) (0.016 g), m.p. 100—102 °C (from ethyl acetate–methanol); $[\alpha]_D$ +27° (*c* 0.5); $\nu_{max.}$ 1 670 (CO) and 1 620 cm^{-1} (C=C); $\lambda_{max.}$ 243 nm (log ε 4.02); δ 0.69 (3 H, s, 13-Me), 1.06 (3 H, s, 10-Me), and 6.82 (1 H, br s, 4′-H) (Found: C, 84.6; H, 11.3%; M^+, 424. $C_{30}H_{48}O$ requires C, 84.9; H, 11.4%; *M*, 424).

4α,5α-*Dihydrobenzo*[4,5,6]*cholest*-4-*en*-5′(6′H)-*one* (10).—(a) The hydroxy ketone (7) (1.5 g) in ethanolic 0.4M-potassium hydroxide (250 ml) was refluxed under nitrogen for 7 h. Solid CO_2 was added and the product was isolated by extraction with benzene, and purified by preparative h.p.l.c. with ethyl acetate–benzene (1 : 9), to give the *enone* (10) (1.1 g), m.p. 121—123 °C (from acetone–methanol); $[\alpha]_D$ +139° (*c* 1.4); $\nu_{max.}$ 1 654 cm^{-1} (CO); $\lambda_{max.}$ 254 (log ε 4.03) and 248 (log ε 4.07) nm; δ 0.66 (3 H, s, 13-Me), 0.92 (3 H, s, 10-Me), and 6.95 (1 H, s, 4′-H) (Found: 85.0; H, 11.5%; M^+, 424. $C_{30}H_{48}O$ requires C, 84.9; H, 11.4%; *M*, 424).

(b) A solution of the 5β-Δ^6-5′-ketone (8) and toluene-*p*-sulphonic acid (8 mg) in benzene (1 ml) was refluxed under nitrogen for 4 h. Sodium hydrogen carbonate was added and the product was isolated by extraction with benzene to give the enone (10) (6 mg), m.p. and mixed m.p. 120—122 °C (from acetone–methanol).

(c) The 5β-$\Delta^{6(4')}$-5′-ketone (9) (4.1 mg) was treated with ethanolic 0.2M-potassium hydroxide (1 ml) for 1 h. Solid CO_2 was added, and the product was isolated by extraction with benzene and chromatographed on silica gel (3 g) to give the 5α-isomer (10) (1.5 mg), m.p. and mixed m.p. 120—123 °C.

Crystallographic Analysis.—Suitable single crystals of (9) and (10) were selected, after standard photographic examination, for data collection on a Phillips PW1100 diffractometer, using graphite-monochromated radiation. Accurate cell parameters were obtained in each case from the least-squares

refinement of the setting angles of 25 measured reflections. The crystal data and details of the crystallographic analysis are listed in Table 4. Both structures were solved by MULTAN 78 [16] and refined by blocked-matrix least-squares methods with σ_F^{-2} weight, using the program SHELX.[17] All hydrogen atoms were located using difference Fourier maps, and their parameters were included in the refinements. Using anisotropic thermal parameters for the non-hydrogen atoms and common isotropic thermal parameters for the hydrogen atoms, convergence was reached at $R_w = 0.055$ for (9) and $R_w = 0.069$ for (10). All the data were used in the refinements. The final atomic co-ordinates are listed in Table 5, and the puckering parameters [13] and the descriptions [14] of the ring conformations are listed in Table 3. Observed bond lengths and angles, and endocyclic torsion angles are given in Tables 6—8. Thermal parameters and structure factors are listed in Supplementary Publication No. SUP 23789 (13 pp.).*

* For details of the Supplementary Publication Scheme see *Instructions for Authors* (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, issue 1.

Table 4. Crystal data for compounds (9) and (10)

	(9)	(10)
Formula	$C_{30}H_{48}O$	$C_{30}H_{48}O$
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	27.957	27.706
b/Å	12.091	12.608
c/Å	7.943	7.578
U/Å^3	2 685	2 647
Z	4	4
D_c/g cm^{-3}	1.05	1.06
Radiation	Cu-K_α	Mo-K_α
μ/cm^{-1}	3.90	0.31
Scan width/°θ	1.60	1.10
θ-range	$6 \leqslant \theta \leqslant 60$	$3 \leqslant \theta \leqslant 23$
Reflections measured	2 283	2 484
Unobserved reflections [$I < 2\sigma(I)$]	207	1 040
U_{11}-Hydrogen/Å	0.106	0.076
Background peak/ e Å^{-3}	0.22	0.32
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.068	0.110
$R_w = \Sigma w\|\Delta F\|/\Sigma w\|F_o\|$	0.069	0.055

Table 5a. Fractional atomic co-ordinates (× 10^4) of the non-hydrogen atoms, with estimated standard deviations in parentheses

	(9)			(10)		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
C(1)	7 755(2)	6 384(4)	6 992(8)	6 827(2)	2 372(4)	6 944(6)
C(2)	8 205(2)	6 602(5)	7 937(11)	7 270(2)	2 378(5)	8 116(8)
C(3)	8 334(2)	7 771(5)	7 844(8)	7 445(2)	3 457(4)	8 569(8)
C(4)	7 916(1)	8 549(3)	7 454(5)	7 046(2)	4 161(4)	9 410(7)
C(5)	7 467(1)	8 184(3)	8 357(4)	6 568(2)	4 080(4)	8 330(6)
C(6)	7 076(1)	9 046(3)	8 154(4)	6 161(2)	4 653(3)	9 160(6)
C(7)	6 571(2)	8 678(3)	8 285(5)	5 744(2)	4 865(4)	8 009(6)
C(8)	6 452(1)	7 684(3)	7 090(5)	5 580(2)	3 843(3)	7 032(6)
C(9)	6 910(1)	7 152(3)	6 435(5)	6 003(2)	3 188(3)	6 304(6)
C(10)	7 295(1)	6 995(3)	7 822(5)	6 396(2)	2 967(4)	7 726(6)
C(11)	6 785(2)	6 122(3)	5 412(6)	5 815(2)	2 202(4)	5 378(6)
C(12)	6 441(1)	6 392(3)	3 957(5)	5 449(2)	2 477(4)	3 850(6)
C(13)	5 985(1)	6 973(3)	4 537(5)	5 030(2)	3 144(3)	4 536(6)
C(14)	6 147(1)	7 998(3)	5 583(5)	5 242(2)	4 106(3)	5 503(6)
C(15)	5 680(2)	8 648(3)	5 821(6)	4 806(2)	4 835(4)	5 842(6)
C(16)	5 418(2)	8 471(3)	4 142(7)	4 485(2)	4 641(3)	4 223(6)
C(17)	5 686(1)	7 544(3)	3 153(5)	4 712(2)	3 713(3)	3 148(6)
C(18)	5 668(2)	6 187(4)	5 572(6)	4 702(2)	2 483(4)	5 741(6)
C(19)	7 099(2)	6 370(4)	9 343(7)	6 184(2)	2 280(3)	9 212(6)
C(20)	5 352(1)	6 858(3)	2 047(5)	4 337(2)	3 087(4)	2 131(6)
C(21)	5 612(2)	5 913(4)	1 119(6)	4 553(2)	2 123(4)	1 128(6)
C(22)	5 081(2)	7 596(3)	780(6)	4 058(2)	3 808(4)	797(7)
C(23)	4 702(2)	7 012(4)	−2 45(6)	3 662(2)	3 257(4)	−230(7)
C(24)	4 401(2)	7 802(4)	−1 286(7)	3 396(2)	3 982(4)	−1 445(7)
C(25)	4 007(2)	7 258(5)	−2 337(7)	2 995(2)	3 483(4)	−2 531(7)
C(26)	4 212(2)	6 582(5)	−3 769(7)	3 180(3)	2 560(6)	−3 672(11)
C(27)	3 655(3)	8 085(6)	−2 963(12)	2 699(3)	4 286(7)	−3 576(11)
C(4′)	7 182(2)	10 110(3)	7 854(5)	6 167(2)	4 950(4)	10 934(7)
C(5′)	7 679(2)	10 528(3)	7 754(5)	6 556(2)	4 664(5)	12 090(8)
C(6′)	8 062(2)	9 716(4)	7 961(6)	6 962(2)	3 964(5)	11 390(8)
O(1)	7 746(2)	11 527(2)	7 537(5)	6 578(1)	4 993(3)	13 639(5)

Table 5b. Fractional atomic co-ordinates (× 10^3) of the hydrogen atoms, with estimated standard deviations in parentheses

	(9)			(10)		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
H(1A)	776(1)	646(4)	545(6)	692(1)	261(3)	605(5)
H(1B)	763(1)	556(3)	732(6)	670(1)	152(3)	663(6)
H(2A)	843(1)	603(3)	741(6)	751(1)	202(3)	783(5)
H(2B)	799(1)	642(3)	949(5)	718(1)	193(3)	935(6)
H(3A)	859(1)	776(3)	702(6)	751(1)	387(3)	734(5)
H(3B)	842(1)	806(3)	942(5)	782(1)	374(3)	932(5)
H(4)	781(1)	858(3)	606(6)	717(1)	507(3)	963(5)

Table 5b *(continued)*

Atom	(9) x/a	y/b	z/c	(10) x/a	y/b	z/c
H(5)	757(1)	817(3)	941(5)	668(2)	447(3)	729(5)
H(7A)	637(1)	931(3)	797(6)	540(1)	534(3)	823(6)
H(7B)	651(1)	848(3)	955(6)	576(1)	535(3)	685(5)
H(8)	626(1)	719(3)	785(6)	540(1)	337(3)	766(5)
H(9)	704(1)	771(3)	568(5)	612(1)	370(3)	550(6)
H(11A)	703(1)	575(4)	505(6)	613(1)	178(3)	487(6)
H(11B)	668(1)	554(3)	605(5)	564(1)	169(3)	616(6)
H(12A)	659(1)	696(3)	326(5)	559(1)	294(3)	324(6)
H(12B)	639(1)	569(3)	344(5)	535(1)	178(3)	329(6)
H(14)	634(1)	842(3)	484(5)	544(1)	450(3)	475(6)
H(15A)	580(1)	943(3)	576(6)	488(1)	556(3)	609(5)
H(15B)	545(1)	848(3)	685(6)	468(1)	456(3)	670(6)
H(16A)	532(1)	919(3)	358(5)	439(1)	538(3)	328(6)
H(16B)	504(1)	821(4)	415(5)	416(1)	452(3)	465(6)
H(17)	596(1)	790(3)	237(5)	499(1)	410(3)	211(5)
H(18A)	587(1)	591(3)	651(5)	459(1)	173(3)	516(6)
H(18B)	552(1)	557(4)	506(6)	495(1)	224(3)	692(5)
H(18C)	532(1)	645(3)	595(6)	433(1)	244(3)	562(5)
H(19A)	681(1)	684(3)	998(6)	601(1)	152(3)	877(5)
H(19B)	742(1)	628(3)	1 009(5)	594(1)	262(3)	960(5)
H(19C)	696(1)	562(3)	888(5)	647(1)	203(3)	1 011(6)
H(20)	505(1)	659(3)	280(6)	403(1)	291(3)	260(5)
H(21A)	576(1)	535(3)	208(6)	474(2)	156(3)	146(6)
H(21B)	592(1)	609(4)	55(6)	426(1)	158(3)	79(5)
H(21C)	538(1)	557(4)	16(5)	483(1)	239(3)	53(5)
H(22A)	531(1)	800(3)	7(5)	394(1)	466(3)	−40(6)
H(22B)	492(1)	810(3)	158(5)	431(1)	406(3)	15(6)
H(23A)	483(1)	641(3)	−106(6)	340(1)	298(3)	59(5)
H(23B)	446(1)	671(3)	68(5)	378(1)	245(3)	−31(6)
H(24A)	457(2)	833(4)	−198(6)	363(1)	433(3)	−204(5)
H(24B)	420(2)	813(4)	−44(6)	329(1)	489(3)	−128(5)
H(25)	382(2)	652(4)	−150(6)	280(1)	301(3)	−197(5)
H(26A)	388(2)	625(4)	−457(6)	287(1)	211(3)	−469(6)
H(26B)	433(2)	719(4)	−444(6)	327(2)	180(3)	−274(6)
H(26C)	451(1)	585(4)	−324(6)	328(2)	315(4)	−423(7)
H(27A)	386(2)	863(4)	−388(6)	268(1)	507(4)	−286(6)
H(27B)	340(2)	760(3)	−362(6)	234(1)	363(3)	−389(6)
H(27C)	365(2)	862(4)	−230(7)	297(2)	446(4)	−460(6)
H(4′)	691(1)	1 066(4)	768(6)	595(2)	547(3)	1 172(6)
H(6′A)	842(2)	994(3)	730(6)	689(2)	323(3)	1 124(6)
H(6′B)	813(1)	961(4)	942(6)	735(2)	424(3)	1 196(6)

Table 6. Bond lengths (Å) of bonds between non-hydrogen atoms, with estimated standard deviations in parentheses

Bond	(9)	(10)
C(1)–C(2)	1.488(9)	1.516(7)
C(1)–C(10)	1.624(7)	1.529(7)
C(2)–C(3)	1.461(8)	1.484(8)
C(3)–C(4)	1.532(6)	1.555(8)
C(4)–C(5)	1.512(5)	1.559(7)
C(4)–C(6′)	1.523(6)	1.539(8)
C(5)–C(6)	1.518(5)	1.481(7)
C(5)–C(10)	1.575(5)	1.551(7)
C(6)–C(7)	1.483(6)	1.472(7)
C(6)–C(4′)	1.341(5)	1.396(7)
C(7)–C(8)	1.568(5)	1.553(6)
C(8)–C(9)	1.523(5)	1.537(6)
C(8)–C(14)	1.518(5)	1.526(6)
C(9)–C(10)	1.552(5)	1.556(6)
C(9)–C(11)	1.528(5)	1.520(6)
C(10)–C(19)	1.526(7)	1.538(6)
C(11)–C(12)	1.538(6)	1.577(7)
C(12)–C(13)	1.528(5)	1.525(7)
C(13)–C(14)	1.559(5)	1.534(6)
C(13)–C(17)	1.544(5)	1.548(6)
C(13)–C(18)	1.538(6)	1.533(6)
C(14)–C(15)	1.535(5)	1.541(6)
C(15)–C(16)	1.536(7)	1.535(6)
C(16)–C(17)	1.560(6)	1.558(6)

Table 6 *(continued)*

Bond	(9)	(10)
C(17)–C(20)	1.528(6)	1.516(6)
C(20)–C(21)	1.543(6)	1.553(7)
C(20)–C(22)	1.543(6)	1.564(7)
C(22)–C(23)	1.512(6)	1.514(7)
C(23)–C(24)	1.518(7)	1.493(7)
C(24)–C(25)	1.530(8)	1.518(8)
C(25)–C(26)	1.513(8)	1.537(9)
C(25)–C(27)	1.489(9)	1.525(10)
C(4′)–C(5′)	1.482(7)	1.525(9)
C(5′)–C(6′)	1.462(7)	1.436(8)
C(5′)–O(1)	1.234(5)	1.247(7)

Table 7. Bond angles (°) for non-hydrogen atoms, with estimated standard deviations in parentheses

Atoms	(9)	(10)
C(2)–C(1)–C(10)	112.6(5)	113.8(4)
C(1)–C(2)–C(3)	110.8(5)	113.9(5)
C(2)–C(3)–C(4)	114.6(4)	112.7(4)
C(3)–C(4)–C(5)	111.0(3)	110.5(4)
C(3)–C(4)–C(6′)	108.2(4)	114.5(5)
C(5)–C(4)–C(6′)	111.5(3)	111.9(4)
C(4)–C(5)–C(6)	110.3(3)	113.1(4)
C(4)–C(5)–C(10)	113.0(3)	118.4(4)

Table 7 (*continued*)

Atoms	(9)	(10)
C(6)–C(5)–C(10)	112.3(3)	109.4(4)
C(5)–C(6)–C(7)	118.1(3)	115.8(4)
C(5)–C(6)–C(4′)	121.3(4)	122.1(4)
C(7)–C(6)–C(4′)	120.6(4)	122.1(4)
C(6)–C(7)–C(8)	113.0(3)	111.1(4)
C(7)–C(8)–C(9)	110.6(3)	113.2(4)
C(7)–C(8)–C(14)	113.9(3)	111.2(3)
C(9)–C(8)–C(14)	108.0(3)	108.2(3)
C(8)–C(9)–C(10)	113.1(3)	112.4(4)
C(8)–C(9)–C(11)	109.4(3)	110.1(4)
C(10)–C(9)–C(11)	115.9(3)	114.5(4)
C(1)–C(10)–C(5)	106.5(3)	108.6(4)
C(1)–C(10)–C(9)	108.5(4)	111.4(4)
C(5)–C(10)–C(9)	106.9(3)	105.0(4)
C(1)–C(10)–C(19)	112.4(4)	107.8(4)
C(5)–C(10)–C(19)	110.3(3)	114.3(4)
C(9)–C(10)–C(19)	112.0(3)	109.9(4)
C(9)–C(11)–C(12)	111.7(3)	112.3(4)
C(11)–C(12)–C(13)	113.1(3)	111.1(4)
C(12)–C(13)–C(14)	106.5(3)	107.9(4)
C(12)–C(13)–C(17)	116.3(3)	117.2(4)
C(12)–C(13)–C(18)	111.0(3)	110.7(4)
C(14)–C(13)–C(17)	100.4(3)	100.1(3)
C(14)–C(13)–C(18)	111.9(3)	111.9(4)
C(17)–C(13)–C(18)	110.2(3)	108.6(4)
C(8)–C(14)–C(13)	112.6(3)	115.2(3)
C(8)–C(14)–C(15)	120.6(3)	118.9(4)
C(13)–C(14)–C(15)	103.0(3)	104.5(4)
C(14)–C(15)–C(16)	103.1(3)	103.0(4)
C(15)–C(16)–C(17)	108.0(3)	107.7(4)
C(13)–C(17)–C(16)	102.9(3)	102.9(3)
C(13)–C(17)–C(20)	119.9(3)	119.6(4)
C(16)–C(17)–C(20)	112.7(3)	112.3(4)
C(17)–C(20)–C(21)	112.8(3)	113.1(4)
C(17)–C(20)–C(22)	111.2(3)	111.4(4)
C(21)–C(20)–C(22)	110.4(4)	109.2(4)
C(20)–C(22)–C(23)	115.1(4)	115.0(4)
C(22)–C(23)–C(24)	112.8(4)	113.2(4)
C(23)–C(24)–C(25)	115.2(4)	116.2(4)
C(24)–C(25)–C(26)	111.8(4)	112.0(5)
C(24)–C(25)–C(27)	111.7(5)	113.5(5)
C(26)–C(25)–C(27)	111.2(6)	112.9(5)
C(4)–C(6′)–C(5′)	113.4(4)	110.9(5)
C(4′)–C(5′)–C(6′)	116.9(4)	119.2(5)
O(1)–C(5′)–C(4′)	119.0(5)	121.8(6)
O(1)–C(5′)–C(6′)	124.2(5)	118.9(5)
C(6)–C(4′)–C(5′)	122.9(4)	121.9(5)

Table 8. Endocyclic torsion angles (°) with estimated standard deviations in parentheses

Atoms	(9)	(10)
C(10)–C(1)–C(2)–C(3)	−65.3(5)	−57.6(5)
C(1)–C(2)–C(3)–C(4)	22.5(5)	54.5(5)
C(2)–C(3)–C(4)–C(5)	38.9(5)	−46.6(5)
C(3)–C(4)–C(5)–C(10)	−61.2(5)	44.7(5)
C(4)–C(5)–C(10)–C(1)	20.0(5)	−46.1(5)
C(5)–C(10)–C(1)–C(2)	41.3(5)	50.1(5)
C(10)–C(5)–C(6)–C(7)	27.6(5)	−62.2(5)
C(5)–C(6)–C(7)–C(8)	−52.6(5)	49.9(5)
C(6)–C(7)–C(8)–C(9)	14.8(5)	−43.1(5)
C(7)–C(8)–C(9)–C(10)	43.9(5)	50.9(5)
C(14)–C(8)–C(9)–C(11)	−60.1(5)	−56.6(5)
C(8)–C(9)–C(10)–C(5)	−67.6(5)	−59.3(5)
C(9)–C(10)–C(5)–C(6)	29.7(5)	63.1(4)

Table 8 (*continued*)

Atoms	(9)	(10)
C(8)–C(9)–C(11)–C(12)	56.8(5)	56.8(5)
C(9)–C(11)–C(12)–C(13)	−55.1(5)	−55.9(4)
C(11)–C(12)–C(13)–C(14)	53.5(5)	53.1(5)
C(12)–C(13)–C(14)–C(8)	−59.0(5)	−57.8(5)
C(13)–C(14)–C(8)–C(9)	63.5(5)	59.4(5)
C(17)–C(13)–C(14)–C(15)	47.9(5)	46.7(5)
C(13)–C(14)–C(15)–C(16)	−36.5(5)	−33.5(5)
C(14)–C(15)–C(16)–C(17)	11.5(5)	7.2(5)
C(15)–C(16)–C(17)–C(13)	18.0(5)	21.1(5)
C(16)–C(17)–C(13)–C(14)	−39.5(5)	−40.7(5)
C(4′)–C(6)–C(5)–C(4)	−24.9(5)	−17.9(6)
C(6)–C(5)–C(4)–C(6′)	51.5(5)	45.6(5)
C(5)–C(4)–C(6′)–C(5′)	−53.8(5)	−51.6(5)
C(4)–C(6′)–C(5′)–C(4′)	26.6(5)	31.4(5)
C(6′)–C(5′)–C(4′)–C(6)	1.4(5)	−3.4(6)
C(5′)–C(4′)–C(6)–C(5)	−2.0(5)	−3.7(6)

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