Steroidal Sulphur Compounds. Part X.[1] Chiroptical Properties of Steroidal Allyl Sulphoxides

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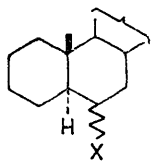
The chiroptical properties of eight steroidal allyl sulphoxides were markedly influenced by the relative spatial orientation of the olefinic double bond and the sulphoxide group, and chirality at sulphur did not necessarily play a predominant role. The influence of solvent upon the chiroptical spectra of some of the sulphoxides depended upon chirality at sulphur.

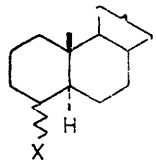
THE isolation of optically active natural products has usually stimulated interest in their chiroptical properties, and, because of the potential facilitation of configurational correlations, in those of structurally related compounds. However, information concerning the chiroptical properties of allyl alkyl sulphoxides is scant and conflicting despite the isolation of (+)-*S*-allyl-L-cysteine *S*-oxide[2] (alliin, the precursor of a compound with antibiotic properties)[3] from garlic in 1948. The c.d. curves in water of (+)-*S*-allyl-L-cysteine *S*-oxide and (+)-*S*-propyl-L-cysteine *S*-oxide, which have been allocated the same configuration at sulphur,[4] were found by Scopes and her associates to be similar,[5] although Henson and Mislow had earlier reported them to be almost enantiomeric and therefore apparently indicative of a profound perturbation of the chiroptical properties of the sulphoxide chromophore by the allyl group.[4] However, other data[6] suggest that this perturbation is not general, and that allyl methyl and propyl methyl sulphoxide of equivalent configuration should display Cotton effects of the same sign in water. The chiroptical properties of allyl alkyl sulphoxides were shown to be more solvent-dependent than those of dialkyl sulphoxides.[6b] In order to clarify and augment the available data we have investigated the chiroptical properties of the steroidal allyl sulphoxides (I)—(VIII), which were chosen with the expectation that elucidation of the relationship between structure and chiroptical properties in these compounds would be facilitated by the ease in determining their absolute configuration, and by their conformational rigidity.

(*R*)- and (*S*)-6β-Allylsulphinyl-5α-cholestane (I) and (II) were prepared by treatment of 6β-mercapto-5α-cholestane (IX) with sodium ethoxide and allyl bromide to give the 6β-allyl sulphide (X), which was then oxidised with peroxydodecanoic acid. The sulphoxides (I) and (II) were separated chromatographically, and on further oxidation they both gave the same sulphone (XI), confirming that they differed only in configuration at sulphur. The sulphoxides were configurationally stable at room temperature, but in benzene at 56° they underwent equilibration at sulphur to give a mixture of (I) and (II) in which the former slightly predominated. The ready thermal stereomutation of allyl sulphoxides is well documented.[7] Reduction of the sulphoxides (I) and (II) separately



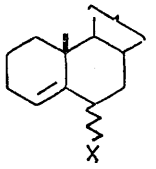
X

(I) 6β-(*R*)-S(O)·$CH_2CH{:}CH_2$
(II) 6β-(*S*)-S(O)·$CH_2CH{:}CH_2$
(IX) 6β-SH
(X) 6β-S·CH_2·$CH{:}CH_2$
(XI) 6β-SO_2·CH_2·$CH{:}CH_2$
(XII) 6β-(*R*)-S(O)·CH_2·CH_2·CH_3
(XIII) 6β-(*S*)-S(O)·CH_2·CH_2·CH_3
(XV) 6β-(*R*)-S(O)·CH_3
(XVI) 6β-(*S*)-S(O)·CH_3
(XVII) 6α-(*S*)-S(O)·CH_3



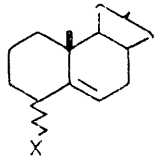
X

(XVIII) 4β-(*R*)-S(O)·CH_3
(XIX) 4β-(*S*)-S(O)·CH_3
(XX) 4α-(*R*)-S(O)·CH_3



X

(III) 6β-(*R*)-S(O)·CH_3
(IV) 6β-(*S*)-S(O)·CH_3
(V) 6α-(*S*)-S(O)·CH_3
(XIV) 6α-S·CH_3



X

(VI) 4β-(*R*)-S(O)·CH_3
(VII) 4β-(*S*)-S(O)·CH_3
(VIII) 4α-(*R*)-S(O)·CH_3

with di-imide gave the known[8] (*R*)- and (*S*)-6β-propylsulphinyl-5α-cholestanes (XII) and (XIII), respectively,

[1] Part IX, D. N. Jones, J. Blenkinsopp, A. C. F. Edmonds, E. Helmy, and R. J. K. Taylor, *J.C.S. Perkin I*, 1973, 2602; preliminary communication, D. N. Jones, E. Helmy, R. J. K. Taylor, and A. C. F. Edmonds, *Chem. Comm.*, 1971, 1401.

[2] A. Stoll and E. Seebeck, *Helv. Chim. Acta*, 1948, **31**, 189.

[3] C. J. Cavallito, J. S. Buck, and C. M. Suter, *J. Amer. Chem. Soc.*, 1944, **66**, 1952; A. Stoll and E. Seebeck, *Helv. Chim. Acta*, 1949, **32**, 197; A. Stoll and E. Seebeck, *Adv. Enzymol.*, 1951, **11**, 377.

[4] P. D. Henson and K. Mislow, *Chem. Comm.*, 1969, 413.

[5] L. Fowden, P. M. Scopes, and R. N. Thomas, *J. Chem. Soc.* (*C*), 1971, 833.

[6] (*a*) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, *J. Amer. Chem. Soc.*, 1965, **87**, 1958; (*b*) M. Axelrod, P. Bickart, M. L. Goldstein, M. M. Green, A. Kjaer, and K. Mislow, *Tetrahedron Letters*, 1968, 3249.

[7] P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4869; R. Tang and K. Mislow, *ibid.*, 1970, **92**, 2100.

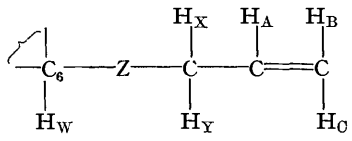
[8] D. N. Jones, D. Mundy, and R. D. Whitehouse, *J. Chem. Soc.* (*C*), 1969, 1668.

thus establishing the configurations of the allyl sulphoxides (I) and (II). The preparation of the sulphoxides (III)—(VIII) has been described previously.[1]

The n.m.r. spectra (Table 1) of the sulphoxides (I) and (II) were consistent with the structures allocated,[9] each displaying signals attributable to three vinyl protons with reasonable values for the appropriate coupling constants,[9] and signals due to a CH_2·S(O) group. The spectra were readily amenable to first-order analysis, there being no problems due to the overlapping of signals. They showed that prototropy to the propenylsulphinyl system, which can occur under some circumstances,[10] had not occurred during the manipulation of these compounds; it was important to establish this fact in order to ensure the validity of the subsequent chiroptical investigation. A feature of the spectra was the fact that the diastereotopic methylene protons of the allyl group in the (*S*)-sulphoxide (II) and the sulphone (XI) were anisochronous, whereas they were isochronous in the (*R*)-sulphoxide (I) and the sulphide (X). The n.m.r. spectra of (I) and (II) also shared features in common with those of many (*R*)- and (*S*)-6β-alkylsulphinyl-5α-cholestanes,[8] so that evidence was provided for the preferred conformations of (I) and (II) with respect to rotation about the C(6)–S bond. In particular, the 10-methyl group in the (*R*)-6β-allyl sulphoxide (I) resonated 12 Hz to higher field than the 10-methyl group in the (*S*)-isomer (II), and the 6α-proton was progressively less shielded in the 6β-allyl sulphide (X), the (*R*)-6β-sulphoxide (I), the (*S*)-6β-sulphoxide (II), and the 6β-sulphone (XI). By analogy with arguments presented in detail elsewhere[8] this behaviour may be attributed to the influence of the acetylenic-type anisotropy of the sulphinyl bond in the preferred conformations (A) and (B) of the (*R*)- and (*S*)-6β-allyl sulphoxides (I) and (II), respectively. The n.m.r. spectra did not reveal the preferred conformations of the allyl system with respect to the sulphinyl group (a knowledge of which would facilitate interpretation of the chiroptical properties) but it is unlikely that the preferred conformations of (I) and (II) involve an '*s-cis*' arrangement (C) of the vinyl group and the S–C(1′) bond. We believe this is so because oxidation of 6β-allylthio-5α-cholestane to (I) and (II) was attended by downfield shifts of 28—38 Hz in the terminal vinyl signals, whereas oxidation of the 6α-sulphide (XIV) to the sulphoxide (V), which exists in the conformation (C), was attended by an upfield shift of 35 Hz in the vinyl proton signal.[1]

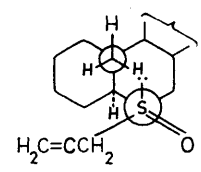
TABLE 1

N.m.r. data for 6β-allylthio-5α-cholestane and its derivatives *



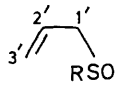
		Band positions (τ values)								J/Hz					
Compound	Z	10-Me	13-Me	H_A	H_B	H_C	H_X	H_Y	H_W	($W_{\frac{1}{2}}$/Hz)	J_{AB}	J_{AC}	J_{BC}	J_{AX}	J_{AY}	J_{XY}
(X)	S	9·09	9·31	4·26	4·99	4·98	6·98	6·98	7·27	(7)	10	17	1	7	7	†
(I)	(*R*)-S(O)	8·94	9·34	4·12	4·63	4·70	6·63	6·63	7·21	(11)	10	16	1·5	7	7	†
(II)	(*S*)-S(O)	8·82	9·34	4·02	4·61	4·69	6·50	6·78	7·09	(7)	9·5	16·5	1·5	7·5	6·5	13
(XI)	SO_2	8·90	9·30	4·05	4·58	4·64	6·30	6·50	6·80	(10)	10	17	1·5	7·5	6	14

* Determined on a Varian HA-100 spectrometer for solutions in $CDCl_3$. † Not observable.

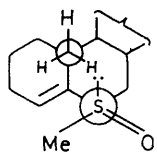


(A)

[B; as (A) with oxygen and allyl group interchanged]

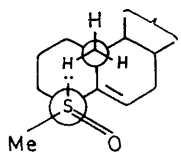


(C)



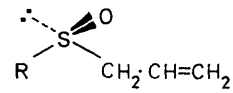
(E)

[F; as (E) with oxygen and methyl group interchanged]



(G)

[H; as (G) with oxygen and methyl group interchanged]



(D)

U.v. spectral data for the allyl sulphoxides (I)—(VIII) are collected in Table 2. Comparison with the u.v. characteristics of their saturated (non-olefinic) counterparts[8,11] indicated that the presence of the double

[9] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, London, 1969, pp. 184, 222, 301.

[10] D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, 1964, **86**, 3840.

[11] D. N. Jones, M. J. Green, and R. D. Whitehouse, *J. Chem. Soc.* (*C*), 1969, 1166.

bond had little effect upon the position of the band near 235 nm, but for (III), (IV), (VI), and (VII) (only) its intensity was significantly enhanced. Whereas the saturated analogues [8,11] of all the sulphoxides (I)—(VIII) displayed discrete maxima near 210 nm, only (I), (II), (III), and (VII) among the unsaturated sulphoxides did so, and these bands were enhanced in intensity; cholest-4-ene, cholest-5-ene, and terminal transitions of the non-bonded electrons of the sulphur atom,[13] but an accurate description of the electronic transitions in allyl sulphoxides is not available (which is not surprising in view of the difficulties associated with the assignment of the electronic transitions of the olefinic double bond [12,14] and sulphoxide group [15] in isolation) so that a rigorous correlation of their chiroptical properties with intramolecular structural features

TABLE 2

C.d. and u.v. data for steroidal allyl sulphoxides

	In hexane				In ethanol			
	c.d.		u.v.		c.d.		u.v.	
	Δε	λ/nm	ε	λ/nm	Δε	λ/nm	ε	λ/nm
(I)	0	270			0	275		
	4·34m	243	1420	240	6·34m	234	1410	230
	0	231			0	221		
	−7·00m	217	8000	210	−7·70m	206		
	0	200			−5·0!	200		
(II)	0	270			0	262		
	−5·70m	241	1650	238	−5·90m	230	1750	228
	0	226			0	216		
	12·10m	211	7700	212	8·20m	204		
	0	198			8·0!	200		
(III)	0	265			0	253		
	11·25m	238	3080	235	3·55m	234	3900	225
	0	222			2·00n	224		
	−15·6m	207	12,100	208	6·43m	213	14,230	206
	−13·7!	203			0	204		
(IV)	0	259			0	255		
	3·75m	232	3140	233	9·71m	225	3760	223
	0	220			0	212		
	−3·65m	208			−7·52!	206		
(V)	0	232			0	230		
	6·51m	215			7·03m	215		
(VI)	0	252			0	252		
	−3·21m	231	3145	233	−11·35m	224	3500	223
	0	218			0	210		
	0·96m	206			3·42!	206		
	0	200						
(VII)	0	265			0	255		
	−15·2m	237	3660	234	−7·05m	231	4000	222
	0	216			−6·87n	224		
	10·3m	206	13,100	205	−15·3!	210	12,150	205
	10·0!	204						
(VIII)	0	270			0	250		
	0·52m	235			−6·2m	210	1360	223
	0	230			−6·04!	208		
	−3·44m	215						
	−2·97!	208						

m = Maximum, n = minimum, ! = no maximum or minimum.

acyclic olefins display u.v. maxima at appreciably shorter wavelengths.[12] These u.v. characteristics suggest that there is an electronic interaction between the double bond and the sulphinyl group, and further that it is a function of their relative spatial disposition. The band near 235 nm for solutions in hexane, which is shifted *ca.* 10 nm to shorter wavelengths on changing to ethanol as solvent, was previously attributed to is precluded. Our approach is therefore empirical in nature.

The c.d. data (Table 2) confirm that the u.v. bands near 235 nm and below 210 nm are both optically active. The bisignate c.d. curve [16] for (*R*)-6β-methylsulphinylcholest-4-ene (III) in hexane was antipodal to that for its (*S*)-isomer (IV), which, in view of the marked influence of the dissymmetric steroid skeleton

[12] A. I. Scott and A. D. Wrixon, *Tetrahedron*, 1970, **26**, 3695; A. I. Scott, ' Interpretation of the Ultraviolet Spectra of Natural Products,' Pergamon, London, 1964, pp. 18, 20.

[13] M. Prochazka and M. Palacek, *Coll. Czech. Chem. Comm.*, 1967, **32**, 3049.

[14] A. F. Drake and S. F. Mason, *J.C.S. Chem. Comm.*, 1973, 253.

[15] G. L. Bendazzoli, F. Bernardi, P. Palmieri, and C. Zauli, *J. Chem. Soc.* (*A*), 1968, 2186.

[16] This term for ' double-humped,' c.d. curves with humps of opposite sign was proposed by W. Klyne at the NATO Advanced Study Institute on Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism (Pisa, 1971). An illustration of the meaning of term is given by D. N. Jones in ' Structure Determination in Organic Chemistry,' ed. W. D. Ollis, MTP International Review of Science, Butterworths University Park Press, London, 1973, vol. 1, p. 85.

upon the chiroptical properties of their saturated analogues, (*R*)-6β-propylsulphinyl-5α-cholestane (XII) ($\Delta\varepsilon_{235}$ +2·8; $\Delta\varepsilon_{215}$ −1·9, in hexane) and (*S*)-6β-propylsulphinyl-5α-cholestane (XIII) ($\Delta\varepsilon_{227}$ +1·8, in hexane),[8] provides convincing evidence that the allylsulphinyl system predominates in determining the chiroptical properties of alkyl allyl sulphoxides. The o.r.d. curve of (II) in ethanol was similar in shape and sign to those given in water by the configurationally related (+)-(*R*)-allyl methyl sulphoxide, (+)-(*R*)-allyl butyl sulphoxide, and the (*S*)-isomer of *S*-allyl-L-cysteine *S*-oxide, suggesting as a general rule that alkyl allyl sulphoxides of stereoformula (D), in which the allyl group is sterically unconstrained, should display o.r.d. curves in hydroxylic solvents typified by that of (II). The significance of the conformational mobility of the allyl group becomes apparent later. (*R*)-6β-Allylsulphinyl-5α-cholestane (I) displayed chiroptical properties essentially similar to those of (*R*)-6β-propylsulphinyl-5α-cholestane (XII), which contrasts with a previous report that *S*-allyl-L-cysteine *S*-oxide and *S*-propyl-L-cysteine *S*-oxide of equivalent configuration at sulphur displayed almost enantiomeric chiroptical properties,[6b] and conforms with the report that the c.d. curves of these cysteine derivatives were similar in sign.[5] Our data did not provide further insight into the role of βγ-unsaturation in determining the chiroptical properties of allyl sulphoxides, however, since the o.r.d. and c.d. curves of (*S*)-6β-propylsulphinyl-5α-cholestane (XIII) were neither similar nor antipodal to those of (*S*)-6β-allylsulphinyl-5α-cholestane (II).

It appears that chirality at sulphur in allyl sulphoxides does not in itself determine the signs of the Cotton effects, since (*R*)-6β-methylsulphinylcholest-4-ene (III) and its (*S*)-isomer (IV) gave bisignate curves similar in sign (but different in intensity) and the (*R*)- and (*S*)-4β-sulphoxides (VI) and (VII) also gave c.d. curves of the same sign; the sulphoxides (III) and (VI), which had the same configuration at sulphur, gave c.d. curves of opposite sign. βγ-Unsaturation is important in causing these phenomena since the saturated analogues of (III) and (IV), (*R*)-6β-methylsulphinyl-5α-cholestane (XV) ($\Delta\varepsilon_{236}$ +3·3; $\Delta\varepsilon_{217}$ −5·1, in hexane) and (*S*)-6β-methylsulphinyl-5α-cholestane (XVI) ($\Delta\varepsilon_{237}$ −0·4; $\Delta\varepsilon_{222}$ +2·3, in hexane), differing only in configuration at sulphur, gave bisignate c.d. curves of opposite sign.[11] This remarkable behaviour is rational if the chiroptical properties of the allyl sulphinyl system are associated predominantly with the relative spatial orientation of the double bond and the lone electron pair on sulphur, since n.m.r. evidence [1] and examination of Dreiding models suggest that this spatial relationship is similar in the preferred conformations (E) and (F) of (*R*)- and (*S*)-6β-methylsulphinylcholest-4-ene (III) and (IV), respectively, and also similar in the preferred conformations (G) and (H) of the (*R*)- and (*S*)-4β-sulphoxides (VI) and (VII); conversely the spatial relationships of the double bond and lone electron pair in (E) and (H) are enantiomeric, and they are also enantiomeric in (F) and (G). In the light of this rationalisation the antipodal chiroptical properties displayed by (*R*)-6β-allylsulphinyl-5α-cholestane (I) and its (*S*)-isomer (II) are indicative of an antipodal relationship between the sulphur lone electron pair and the double bond in the isomers; this is reasonable because the allyl groups in (I) and (II) are subject to little steric constraint, and their preferred conformation with respect to the sulphinyl group should therefore be determined predominantly by configuration at sulphur.

(*R*)-4α-Methylsulphinylcholest-5-ene (VIII) displayed bisignate c.d. curves opposite in sign to those of (*R*)-4β-methylsulphinylcholest-5-ene (VI) and (*R*)-6β-allylsulphinyl-5α-cholestane (I). Since models and n.m.r. spectroscopy suggest that the relative spatial orientation of the double bond and the sulphur lone electron-pair in (VI) is not antipodal to that in (VIII),[1] and the n.m.r. evidence presented earlier suggests that the orientation is not similar in (I) and (VI), it appears that this spatial relationship controls the chiroptical properties of βγ-unsaturated sulphoxides in a complex manner. This phenomenon is perhaps comparable to that found for βγ-unsaturated ketones, the chiroptical properties of which are a sensitive function of the conformational relationship of the keto-group and the double bond.[17] With the evidence at present available it is clearly not feasible to utilise chiroptical data to allocate configuration and conformation to conformationally constrained alkyl allyl sulphoxides.

In contrast to the marked solvent dependence of the chiroptical behaviour of (+)-(*R*)-allyl methyl sulphoxide and (+)-(*R*)-allyl butyl sulphoxide,[6b] the c.d. spectra of (*R*)- and (*S*)-6β-allylsulphinyl-5α-cholestane (I) and (II) were not affected by changing the solvent from hexane to ethanol, except for relatively small changes in intensity, and shifts to shorter wavelengths in the positions of the bands. Such blue-shifts occurred for the c.d. spectra of all the unsaturated sulphoxides (I)—(VIII), and have also been described previously for saturated sulphoxides.[6,8,11] However, the solvent dependence of the c.d. spectra of (*R*)- and (*S*)-6β-methylsulphinylcholest-4-ene (III) and (IV) were markedly influenced by chirality at sulphur. For the (*R*)-isomer (III) and its pseudo-enantiomer (VII) a change in solvent from hexane to ethanol caused a change in sign of the shorter wavelength band and a diminution in intensity of the longer wavelength band, whereas for the (*S*)-isomer (IV) and its pseudoenantiomer (VI) the same solvent change brought about a marked enhancement in the intensity of both bands without changing their sign. We know of no other case where the chiroptical properties of diastereoisomers differing only in the configuration at one chiral centre exhibit such markedly different solvent dependence, and we are unable to comment usefully on the relative import-

[17] K. Mislow in 'Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry,' ed. G. Snatzke, Heyden, London, 1967, p. 162.

ance of solvent-induced alterations in conformational population, of dissymmetric solvation, and of 'inherent' solvent effects in determining these phenomena.*

EXPERIMENTAL

The c.d. spectra of compounds (I)—(IV), (VI), and (VII) were run with a Roussel–Jouan dichrograph 185 for solutions containing *ca.* 0·5—1 mg per ml with a path length of 1 mm. We are indebted to Professor W. Klyne and Dr. P. M. Scopes, Westfield College, London, for these spectra. The o.r.d. spectra of all the sulphoxides, and the c.d. spectra of (V) and (VIII) were run with a Bendix Polarmatic 62 ORD and CD automatic recording instrument at Sheffield. The u.v. spectra were determined with a Cary 14 spectrophotometer. For other experimental directions see Part IX.[1]

6β-*Allylthio-5α-cholestane* (X).—5α-Cholestan-6β-yl thioacetate[18] (1·0 g) was treated with lithium aluminium hydride (300 mg) in boiling ether (250 ml). After 30 min the usual work-up gave 6β-mercapto-5α-cholestane,[19] which was kept in ether under nitrogen (to prevent air-oxidation to the disulphide, which occurred readily) and treated, with stirring, with a solution of sodium (60 mg) in ethanol (30 ml), followed by allyl bromide (3 ml). After a further 16 h the usual work-up gave an oil which was chromatographed (p.l.c.) with light petroleum as developer. The major band was extracted to give 6β-*allylthio-5α-cholestane* (X) (590 mg, 60%) as an oil, $[\alpha]_D$ −33° (*c* 0·5) (Found: C, 81·1; H, 11·8; S, 7·35. $C_{30}H_{52}S$ requires C, 81·0; H, 11·8; S, 7·2%); a minor band of slightly lower R_F gave, on extraction, an oil (50 mg), which was not examined further.

(R)- *and* (S)-6β-*Allylsulphinyl-5α-cholestane* [(I) *and* (II)].—Peroxydodecanoic acid (90% pure; 86 mg, 0·36 mmol) was added to 6β-allylthio-5α-cholestane (X) (160 mg, 0·36 mmol) in light petroleum (35 ml). After 1 h at room temperature the solution was diluted with ether, washed successively with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated. Chromatography (p.l.c.) of the solid residue with ether–light petroleum (1 : 1) as developer gave three bands which were extracted separately to give, first, (S)-6β-*allylsulphinyl-5α-cholestane* (II) (31 mg, 19%) as an oil, $[\alpha]_D$ −10° (*c* 0·7), $\nu_{max.}$ (CCl_4) 1038 cm^{-1} (Found: C, 77·8; H, 11·45; S, 7·15. $C_{30}H_{52}SO$ requires C, 78·2; H, 11·4; S, 6·95%), secondly, (R)-6β-*allylsulphinyl-5α-cholestane* (I), (104 mg, 62%), m.p. 120° (from methanol), $[\alpha]_D$ −39° (*c* 0·85), $\nu_{max.}$ (CCl_4) 1037 cm^{-1} (Found: C, 78·0; H, 11·25; S, 7·0%), and thirdly, 6β-allylsulphonyl-5α-cholestane (XI) (22 mg, 12%) identical with the specimen described later.

* Leading references to solvent-induced changes in chiroptical properties are given in ref. 15.

6β-*Allylsulphonyl-5α-cholestane* (XI).—(*R*)-6β-Allylsulphinyl-5α-cholestane (I) (198 mg, 0·43 mmol) was treated with 3-chloroperbenzoic acid (76 mg, 0·43 mmol) in ether (100 ml) at room temperature for 3 days. The usual work-up gave the *product* (XI) (181 mg, 88%), m.p. 138—139° (from ether–methanol), $[\alpha]_D$ +18° (*c* 0·35), $\nu_{max.}$ (CCl_4) 1130 and 1311 cm^{-1} (Found: C, 75·2; H, 11·2; S, 7·0. $C_{30}H_{52}SO_2$ requires C, 75·6; H, 11·0; S, 6·7%).

Oxidation of (*S*)-6β-allylsulphinyl-5α-cholestane (II) in the same way gave the sulphone (XI), identical spectroscopically, chromatographically, and in m.p. with the previous sample.

Thermal Stereomutation of the Sulphoxides (I) *and* (II).—(*R*)-6β-Allylsulphinyl-5α-cholestane (I) (361 mg) was kept in boiling benzene (25 ml) for 14 h, and the oil obtained after evaporation of the benzene was chromatographed (p.l.c.) on silica, developed with ether–benzene (1 : 4). The two bands were individually extracted with ether, the top band giving the (*R*)-sulphoxide (I) (188 mg, 53%), and the other giving the (*S*)-sulphoxide (II) (139 mg, 39%). The (*S*)-sulphoxide (II) after being kept in boiling benzene overnight gave the same equilibrium mixture of (I) and (II) (t.l.c. and n.m.r. analysis).

Reduction of the Sulphoxides (I) *and* (II) *with Di-imide.*—(*a*) (*R*)-6β-Allylsulphinyl-5α-cholestane (I) (221 mg) in dry ether (10 ml) was stirred with a slurry of potassium azodicarboxylate (3·3 g) in ether (50 ml) at 0°. Propionic acid (3·3 ml) was added dropwise during 1·5 h, and stirring was continued at room temperature for 2·5 h. The mixture was filtered, and the filtrate was washed with aqueous sodium hydrogen carbonate and water, then dried (Na_2SO_4) and evaporated. The oily residue (197 mg) consisted of a mixture of the allyl sulphoxide (I) and (*R*)-6β-propylsulphinyl-5α-cholestane (XII) in approximately equal amounts, according to t.l.c. [on silica; 45 cm plates developed with ether–benzene (1 : 4)] and n.m.r. spectroscopy, and so it was reduced twice successively with di-imide in the above manner to give finally (*R*)-6β-propylsulphinyl-5α-cholestane (XII) (150 mg, 68%), identical spectroscopically and chromatographically with an authentic sample.[8]

(*b*) (*S*)-6β-Allylsulphinyl-5α-cholestane (II) (50 mg) was treated with di-imide in the above manner to give (*S*)-6β-propylsulphinyl-5α-cholestane (XIII) (30 mg, 60%), identical spectroscopically and chromatographically with an authentic specimen.[8]

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