Optical Rotatory Dispersion and Circular Dichroism of Diastereomeric *S*-Allyl-L-cysteine *S*-Oxides

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Summary The perturbing effect of the allyl group on the chiroptical properties of sulphoxides is strikingly manifested in the observation that the diastereomers of *S*-allyl-L-cysteine *S*-oxide and of *S*-n-propyl-L-cysteine *S*-oxide with the same configuration at sulphur have virtually mirror-image o.r.d. and c.d. curves, whereas those with opposite configurations at sulphur have closely matching o.r.d. and c.d. curves.

ALLIIN (I), a naturally occurring amino-acid present in uninjured garlic,[1] has been shown to be (+)-*S*-allyl-L-cysteine *S*-oxide by degradation[1] and by synthesis[2] from L-cysteine. That the configuration of (I) at sulphur is (*S*) is deduced as follows. Reduction of (I) yields (+)-*S*-n-propyl-L-cysteine *S*-oxide, or dihydroalliin (II),[1] also obtained by synthesis from L-cysteine.[2] The o.r.d. curves of (II) and of the diastereoisomer derived from L-cysteine are almost enantiomeric,[3] showing the over-riding effect of sulphoxide chirality in determining the sign of the spectroscopically accessible Cotton effects.[3,4] Also the similarity of the o.r.d. curves of (II) and of (+)-*S*-methyl-L-cysteine *S*-oxide (III) testifies to the correspondence in chiralities at sulphur of these two compounds. Since the absolute configuration at sulphur in (III) is (*S*), as determined by *X*-ray diffraction,[5] it follows that the absolute configuration at sulphur of (I), as well as of (II), is (*S*).

That (I), (II), and (III) are dextrorotatory at the D-line has been taken to be indicative of and consistent with the correspondence in chiralities at sulphur,[5a,6] However, the allyl group has a profoundly perturbing effect on the sulphoxide chromophore:[7] not only are the Cotton effects (iso-octane solution) of the configurationally related (+)-(*R*)-allyl methyl and (−)-(*R*)-ethyl methyl sulphoxides grossly different, but the signs of rotation at the D-line are opposite. The present study was undertaken to scrutinize the chiroptical properties[8] of (I) more closely for any anomaly ascribable to the presence of the allyl group.

(I), (−)-*S*-allyl-L-cysteine *S*-oxide (IV), and (−)-*S*-n-propyl-L-cysteine *S*-oxide (V), were prepared from L-cysteine.[2] O.r.d. curves for the three compounds in water are presented in Figure 1, along with the o.r.d. curve of (II); Figure 2 shows the corresponding c.d. curves.† It is obvious that (I) and (V), and similarly (II) and (IV),† although having opposite signs of rotation at the D-line and opposite configurations at sulphur, nevertheless have closely similar o.r.d. and c.d. curves. In contrast, the o.r.d. and c.d. curves of the pairs with the same sign of rotation at the D-line and the same configuration, *i.e.* (I) and (II),† and (IV) and (V), display virtually mirror-image contours. Each of the four compounds exhibits two Cotton effects of opposite signs, one at 210—220 nm. and the other at 190—200 nm.

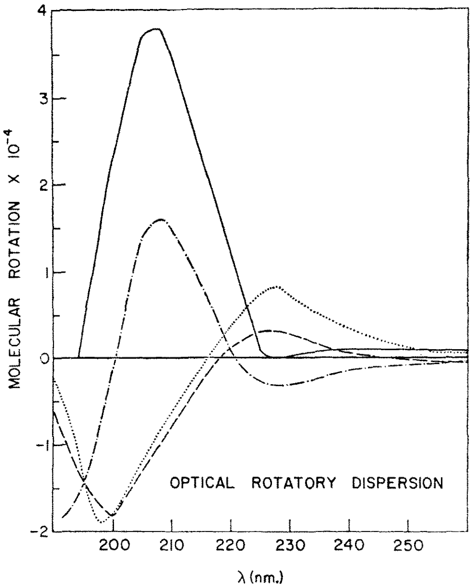

FIGURE 1. *O.r.d. spectra of diastereomeric* S-*allyl- and* S-*n-propyl*-L-*cysteine* S-*oxides in water,* (——) *for* (I), (— — —) *for* (IV), (· · · ·) *for* (II) (*from ref.* 3) *and* (· — · —) *for* (V).

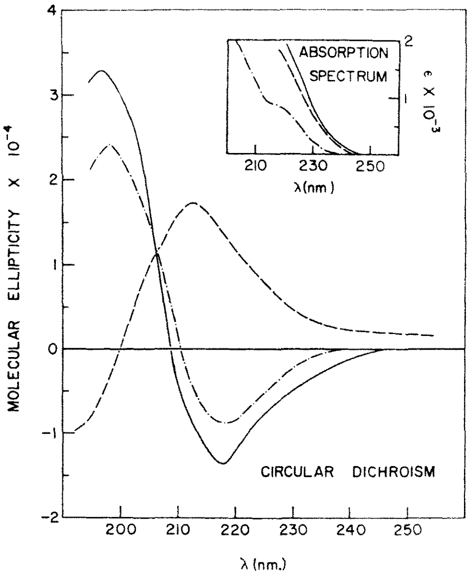

FIGURE 2. *C.d. and absorption spectra of diastereoisomeric* S-*allyl- and* S-*n-propyl*-L-*cysteine* S-*oxides in water. Identification of the curves is the same as in Figure* 1.

Since the sulphoxide chromophore dominates the chiroptical picture,[3,4] this extraordinary behaviour is traceable

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† Because (II) could not be isolated in sufficient purity, the o.r.d. curve presented in Figure 1 is the one previously reported.[3] For the same reason, the c.d. curve of (II) was not recorded.

directly to a perturbation of that chromophore by the allylic π-system. Thus the superficially sensible correspondence between sign of rotation at the D-line and configuration at sulphur in the series of S-alkyl-L-cysteine *S*-oxides [dextrorotation being associated with the (S) and laevorotation with the (*R*) configuration][5a,6] proves to be a treacherous cover of the "allyl effect": in the saturated compounds the sign of rotation at the D-line reflects the sign of the nearest Cotton effect,[3] whereas in the allyl compounds the sign of rotation in the visible region is *opposite* to the sign of the nearest Cotton effect (Figure 1).

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[8] U. Weiss, *Experientia*, 1968, **24**, 1088, has suggested "chiral-optical effects" as a collective term applicable to signed optical properties (such as o.r.d. and c.d.) of chiral systems. We acknowledge the need for such a term but prefer the contraction "chiroptical" (V. Prelog, *Proc., k. ned. Akad. Wetenschap.*, 1968, **71**, *B*, 108).