γ-Radiolysis of *S*-(*cis*-Prop-1-enyl)-L-cysteine in Aqueous Solution: a New *cis*–*trans*-Isomerization of the Prop-1-enyl Thiyl Radicals

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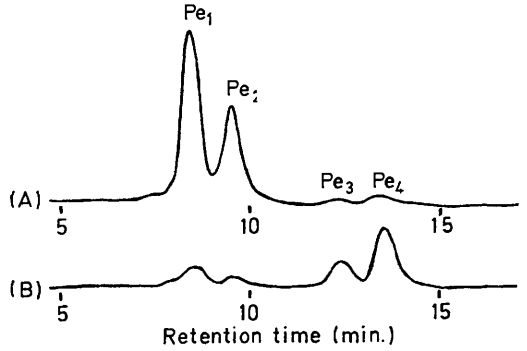
Summary *cis*- and *trans*-Products from γ-irradiated *S*-(*cis*-prop-1-enyl)-L-cysteine are identified and a new isomerization mechanism of the prop-1-enyl thiyl radicals is suggested.

IN connection with flavour deterioration accompanying food irradiation, we have studied the mechanism of formation of volatile products from sulphur-containing amino-acids (precursors of onion and garlic flavour) irradiated by γ-rays in oxygen-free aqueous solutions.[1] The photochemical[2] and radiation-chemical[3] *cis*–*trans*-isomerizations of olefins have been widely investigated in organic solvents and vapour systems. However, radiation-induced *cis*–*trans*-isomerization in aqueous systems has not yet been investigated.

We now report on the identification and mechanism of formation of *cis*- and *trans*-products from *S*-(*cis*-prop-1-enyl)-L-cysteine (a lachrymatory precursor of onion) irradiated in oxygen-free aqueous solution.

S-Allyl-L-cysteine was prepared using a modification of the method of du Vigneaud *et al.*[4] for the production of *S*-methyl-L-cysteine from L-cystine. *S*-(*cis*-Prop-1-enyl)-L-cysteine (PeCS) was prepared by the synthetic procedure of Carson and Wong[5] from *S*-allyl-L-cysteine with Bu^{t}OK in Me$_2$SO; m.p. 179—180° (decomp.); n.m.r. (D$_2$O-NaOD) δ 5·96 (1H, d, J 9 Hz, *cis*-configuration of the double bond); m/e 161 (M^{+}) 116, 88, 87, 74, 41.



Figure

Irradiation was carried out with γ-rays from cobalt-60 of 3 kCi at a dose rate of $6{\cdot}24 \times 10^4$ rad/h at room temperature. The oxygen-free neutral solutions of PeCS (20 mM) dissolved in triply-distilled water were placed in stoppered Pyrex tubes and irradiated to 10^4—10^6 rad.

The gas chromatograms of volatile products from irradiated PeCS (A) and PeCS + 10 mM-NaCN (H radical scavenger)[6] (B) are shown in the Figure.

The combined g.c.–m.s. method† was used to characterize the volatile products and the identity of the products was further confirmed by comparing the m.s. and g.l.c. results with those of reference compounds.‡ From these results, Pe$_1$, Pe$_2$, Pe$_3$, and Pe$_4$ were identified as n-propyl *cis*-prop-1-enyl sulphide, n-propyl *trans*-prop-1-enyl sulphide, *cis,cis*-di-prop-1-enyl sulphide, and *cis,trans*-di-prop-1-enyl sulphide, respectively. No disulphides could be detected using the high sensitivity gas chromatograph.

The radiation-induced decomposition of water in the absence of oxygen is: $H_2O \xrightarrow{\sim\sim\sim} H\cdot,\ e_{aq}^-,\ OH\cdot,\ H_3O^+,\ H_2,\ H_2O_2\cdot$

In order to elucidate the mechanisms involved, PeCS was irradiated after the addition of several scavengers. The yield of alanine decreased with increasing concentration of N$_2$O (specific scavenger for e_{aq}^-)[7] and increased with increasing concentration of KBr (specific scavenger for OH·).[8] Moreover, with increasing concentration of NaCN, Pe$_1$ and Pe$_2$ decreased and Pe$_3$ and Pe$_4$ increased (Figure). Therefore, we consider that PeCS reacts with e_{aq}^- to produce alanine, and the di-prop-1-enyl sulphides may react with H radical to produce n-propyl prop-1-enyl sulphides.

When irradiated at 10^4—10^6 rad, PeCS gave n-propyl prop-1-enyl sulphides in the ratio of *cis* : *trans* = Pe$_1$: Pe$_2$ = 65 : 35 (%), and di-prop-1-enyl sulphides in the ratio of *cis–cis* : *cis–trans* = Pe$_3$: Pe$_4$ = 33 : 67 (%). From this mechanism for the formation of di-prop-1-enyl sulphides, it follows that the proportion of *cis*- and *trans*-prop-1-enyl thiyl radicals is 33 : 67 (%).

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† A. Watson-Biemann (J. T. Watson and K. Biemann, *Annalen*, 1965, **37**, 844) helium separator was used between the gas chromatograph (Hitachi Model K-53 gas chromatograph) and the mass spectrometer (Hitachi Model RMS-4 mass spectrometer).

‡ n-Propyl prop-1-enyl sulphide (*cis* or *trans*) and di-prop-1-enyl sulphide (*cis–cis* or *cis–trans*) were prepared by the treatment of n-propyl allyl sulphide and diallyl sulphide with EtONa in EtOH, respectively. Structures were confirmed by m.s. and i.r.

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