

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.

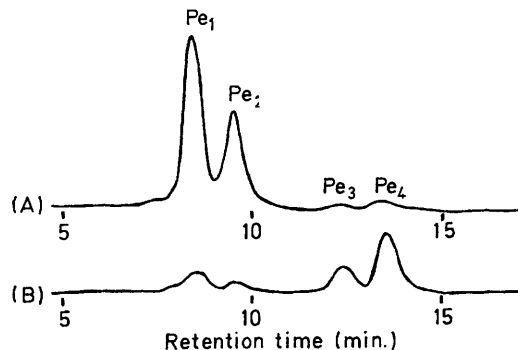
In connection with flavour deterioration accompanying food irradiation, we have studied the mechanism of formation of volatile products from sulphur-containing amino-

acids (precursors of onion and garlic flavour) irradiated by γ -rays in oxygen-free aqueous solutions.¹ The photochemical² and radiation-chemical³ *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 Wong⁵ from *S*-allyl-L-cysteine with Bu^tOK in



FIGURE

Me₂SO; m.p. 179–180° (decomp.); n.m.r. (D₂O–NaOD) δ 5.96 (1H, d, *J* 9 Hz, *cis*-configuration of the double bond); *m/e* 161 (*M*⁺) 116, 88, 87, 74, 41.

Irradiation was carried out with γ -rays from cobalt-60 of 3 kCi at a dose rate of 6.24×10^4 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, Pe₁, Pe₂, Pe₃, and Pe₄ 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: $\text{H}_2\text{O} \xrightarrow{\text{radiation}} \text{H}\cdot, \text{e}_{\text{aq}}^-, \text{OH}\cdot, \text{H}_3\text{O}^+, \text{H}_2, \text{H}_2\text{O}_2$.

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 N₂O (specific scavenger for e_{aq}[–])⁷ and increased with increasing concentration of KBr (specific scavenger for OH[•]).⁸ Moreover, with increasing concentration of NaCN, Pe₁ and Pe₂ decreased and Pe₃ and Pe₄ 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* = Pe₁:Pe₂ = 65:35 (%), and di-prop-1-enyl sulphides in the ratio of *cis-cis:cis-trans* = Pe₃:Pe₄ = 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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