6.5 *The Effects of γ-irradiation on the Garlic Oil Contents in Garlic Bulbs and the Radiolysis of Allyl Trisulfide

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Abstract: The study of the effects of γ-irradiation on the garlic oil contents in the garlic bulbs and the radiolysis of allyl trisulfide and disulfide were carried out. The content of garlic oil in fresh garlic bulbs treated by gamma ray keeps nearly constant as stored for 10 months long. The main components of the garlic oil are allyl trisulfide (about 60%) and allyl disulfide (about 30%). The G values of radiolysis products of allyl disulfide and trisulfide in ethanol system were determined. The results show that allyl trisulfide is a very effective solvated electron scavenger and can oxidize $CH_3C^{\cdot}HOH$ radical into acetaldehyde, which causes that the formation of 2,3-butanediol is extensively inhibited.

Keywords: Garlic, Radiolysis, Allyl Trisulfide, Allyl Disulfide

INTRODUCTION

It is well known that garlic (Allium Sativum) has been used not only for a kind of flavour food but also for wide medical purposes[1,2]. Certain extracts from garlic are of antibacterial and antifungal effects, while other extracts are of antithrombatic, which can inhibit the aggregation of blood platelets. Therefore, a number of researchers have long been attracted by the magic functions of garlic and its products.

Garlic oil is one of the garlic relating active compositions and is composed of garlic decomposing products formed as the garlic was broken into pieces, which can be collected and purified by water steam distillation. Garlic oil is water insoluble, light yellow liquid and mainly composes of allyl disulfide and allyl trisulfide and exhibits a very strong antigerm property. γ-Irradiation can inhibit the sprouting of garlic bulbs in dormancy stage, which is generally used for commercial and marketable purpose. The effects of γ-irradiation on the garlic oil contents in garlic bulbs and the radiolysis of allyl disulfide and trisulfide are rarely reported. In the present work, the reactivities of allyl trisulfide and disulfide with the active species generated by γ irradiation in the ethanol system, such as H, e^-_{solv} and radicals, have been also studied as garlic oil is water insoluble and the radiolysis mechanism of ethanol is almost clear[3,4].

EXPERIMENTS

(1)The contents of garlic oil in bulbs were measured with: (a) steam distillation and extraction methods and (b) $Hg(NO_3)_2$ precipitation method. (2) Allyl disulfide and trisulfide were prepared by Brain Milliger method[5]. The identification and determination of the radiolysis products of disulfide and trisulfide in ethanol system were carried out by GC-MS with different capillary column and detectors for different products. (3) Irradiation samples of disulfide and trisulfide in ethanol were nitrogen saturated and oxygen free.

RESULTS AND DISCUSSION

(1)The effects of γ-irradiation on the contents of garlic oil in bulbs shown in Fig.1, the contents of garlic oil in irradiated bulbs with 50Gy in dormancy stage keep nearly constant during a storage period over 10 months; but in the untreated bulbs the contents fall down when the storage time is over 5 months, meanwhile the bulbs begin to sprout. γ-Irradiation treatment on the sprouted bulbs even with 100Gy is not helpful to prevent the loss of garlic oil. There are about two thirds allyl trisulfide(RSSSR) and one third disulfide(RSSR) of the original quantity in the garlic oil which was obtained with the methods mentioned above.

(2)G values of ethanol radiolysis products in containing RSSR and RSSSR system: the dependence of G values of H_2, CH_3CHO and 2,3-butanediol on the concentrations RSSR and RSSSR are shown in Fig.2 and Fig.3.

As the results shown above, some conclusions could be drawn:

A. G(diol): Both of RSSSR and RSSR can entirely inhibit the formation of 2,3-butanediol even at very low concentrations(about 5×10^{-5} mol dm^{-3}). This indicates that: (a) the precursor of 2,3-butanediol, hydroxyethyl radical was scavenged directly by RSSR and RSSSR or (b) H atom and e-solv was scavenged, which prevented the formation of hydroxyethyl radical.

$$RSSSR + CH_3\dot{C}HOH \longrightarrow RSSH(RSH) + RS\cdot(RSS\cdot) + CH_3CHO \quad (1)$$
$$RSSSR + H^{\cdot} \longrightarrow RSS\cdot(RS\cdot) + RSH(RSSH) \quad (2)$$
$$RSSR + H^{\cdot} \longrightarrow RS\cdot + RSH \quad (3)$$

B. $G(CH_3CHO)$: The G values of CH_3CHO increase very quickly with the concentrations of RSSR and RSSSR and approach their maxima 3.9 and 5.7 respectively. According to the radiolysis mechanism of ethanol, the reason causing the increasing of $G(CH_3CHO)$ is due to the competition of scavenging e^-_{solv} between RSSR/RSSSR and CH_3CHO. The reactions of RSSSR and RSSR with e^-_{solv} are much more fast, which caused the increasing of G value of CH_3CHO.

$$RSSR(RSSSR) + e^-_{solv} \longrightarrow RSSR^-(RSSSR^-) \quad (4)$$
$$CH_3CHO + e^-_{solv} \longrightarrow CH_3CHO^- \quad (5)$$

However, this may be only explainable for the reactivity of RSSR. In the case of RSSSR, there should be another way to form CH_3CHO, because the maximum increase of $G(CH_3CHO)$ caused by the processes mentioned above is only 1.7. So the redox reaction(1) maybe exists and is important to the formation of CH_3CHO in the RSSSR-ethanol system.

C. $G(H_2)$: The values of $G(H_2)$ decrease slowly with the increasing of concentration of RSSSR and RSSR, can not approach 2[3], even [RSSR] and [RSSSR] as high as 10^{-2} mol dm^{-3}. This is reasonable because in the following reaction

$$CH_3CH_2OH + H^{\cdot} \xrightarrow{k_6} CH_3\dot{C}HOH + H_2 \quad (6)$$

k_6 is about 2×10^7 mol^{-1} dm^3 s^{-1}, the ratios of [RSSR] and [RSSSR] to [CH_3CH_2OH] are about

5×10^{-4} , thus reactions (2) and (3) are not comparable to reaction(6) under this condition. In another words, reaction(6) is still predominant over reaction (2) and (3).

(3) The radiolysis products of RSSR and RSSSR in ethanol system.

Irradiated samples were at first separated on GC, three different columns were used, 50m OV-1 capillary column, 25m SE-54 capillary column and 25m PEG-20M capillary column. By comparing the peak retention time with standard compounds on the three columns respectively, and by using FPD detector to check the compounds containing sulfur, and finally GC-MS were used for analysis the structure. The number of sulfur atoms in the molecule can be calculated by using the sulfur M+2 isotope peak intensity. The typical GC and GC-MS spectra are shown in Fig.3-5.

It can be expected that the radiolysis of RSSR and RSSSR should be rather complicated. The G values of main radiolysis products are listed in Tab.1

Tab. 1 The G values of sulfur containing radiolysis products of RSSR and RSSSR in ethanol. Absorbed dose: 4,300 Gy: Dose rate: 1.2 Gy s^{-1}; [RSSR] and [RSSSR] are about 1.0×10^{-3} mol dm^{-3}

Products	-Gc(1)	RSR(F)	RSSR(8)	RSSSR(9)	RSSSSR(K)	RSH(I)
RSSR	1.86	1.02	/	/?	0.10	0.4
RSSSR	2.86	0.2	1.48	/	1.18	1.20

	RS_3H(J)	RS_4H(G)	RS_5H(P)	H_2S(L)	$RSOC_2H_5$(H)	ΔR(%)(2)	ΔS(%)(3)
RSSR	0.2	/	/	1.0	0.40	85.0	90.1
RSSSR	0.15	0.28	0.11	0.90	0.18	88.0	103.0

(1) The total G values of RSSR or RSSSR radiolysis.
(2) The ratio of R (CH_2=CH-CH_2-) in radiolysis products to total R in decomposed RSSR or RSSSR.
(3) The ratio of S in radiolysis products to total S in decomposed RSSR or RSSSR.

The results shown in Tab.1 reveal that the main radiolysis products of RSSR and RSSSR result from attacking S-S bond by reactive species which are induced in the radiolysis of ethanol, such as e^-_{solv}, $H^\cdot$ and $CH_3\dot{C}HOH$, though there are some differences in the G values of the products, and less products from attacking S-C and C=C bonds. This is the reason why the radiolysis product spectrum of trisulfide is more complicated than that of disulfide. From the values of the ΔR and ΔS, it can be seen that there are good material balances of allyl group(R) and sulfur atoms in the radiolysis products. So the radiolysis products of RSSR and RSSSR may be formed through reactions(1)-(4) and following reactions:

$$RSSSR^- + CH_3CH_2OH_2^+ \longrightarrow RSS\cdot(RS\cdot) + RSH(RSSH) + CH_3CH_2OH \quad (7)$$
$$RSSR^- + CH_3CH_2OH_2^+ \longrightarrow RS\cdot(R\cdot) + RSH(RSSH) \quad (8)$$
$$2RSS\cdot \longrightarrow RSSSSR \quad (9)$$
$$2RS\cdot \longrightarrow RSSR \quad (10)$$
$$RS\cdot + C_2H_5O \longrightarrow RSOC_2H_5 \quad (11)$$
$$RSH(RSSH) + H \longrightarrow (RS\cdot) + R\cdot + H_2S \quad (12)$$

CONCLUSION

(1)γ-Irradiation can inhibit the sprouting of garlic bulbs and does not cause the loss of garlic oil yield and the change of the composition of garlic oil in bulbs which have been irradiated during a long period of storage.

(2)Allyl trisulfide and disulfide exhibit strong reactivities to scavenge e^-_{solv}, H and hydroxyethyl radicals introduced by γ-irradiation in the ethanol system, trisulfide can oxidize $CH_3\dot{C}HOH$ radical into acetaldehyde.

(3)The main radiolysis products of RSSSSR(in both cases of trisulfide and disulfide) and RSSR(in trisulfide) can be expected to react with radicals subsequently. Therefore, the garlic oil exhibits remarkable reactivity with radicals.

(4)All of the main radiolysis products are related to the S-S bond breakup, which means that -S-S- is more sensitive to γ-radiation than S-C, C=C and C-H bonds.

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Fig. 1 The Varies of Garlic Oil Contents with Storage Periods

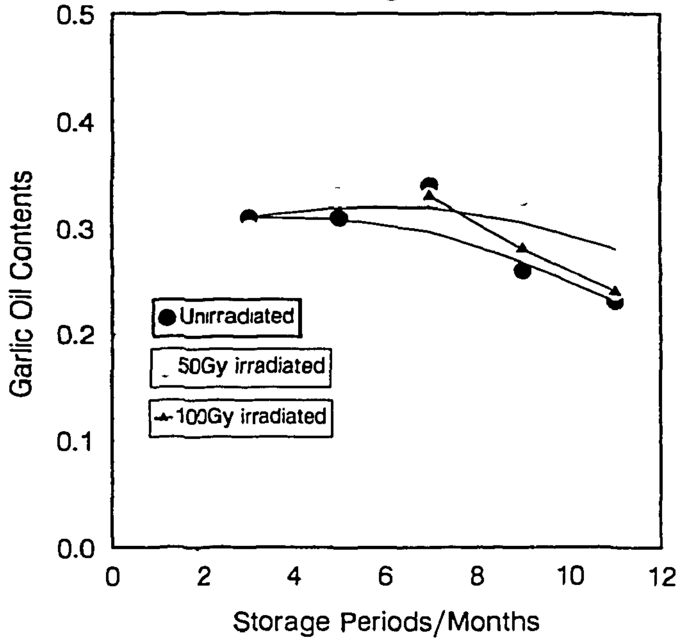


Fig. 2 The dependence of G values of Hydrogen, Acetaldehyde and 2,3-butanediol on [RSSR]; Dose rate=1.2 Gy/s; Absorbed dose=4,300 Gy

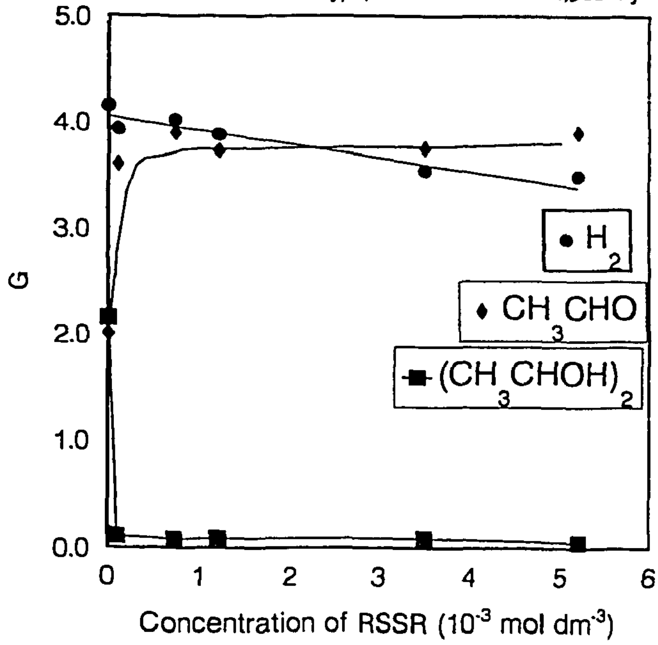
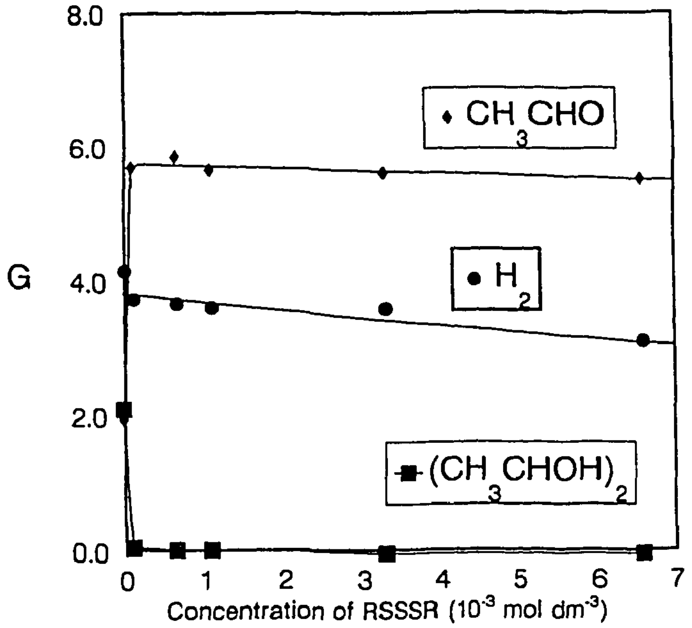


Fig. 3 The dependence of G values of Hydrogen, Acetaldehyde and 2,3-Butanediol on [RSSSR]; Dose rate=1.2 Gy/s; Absorbed dose=4,300Gy



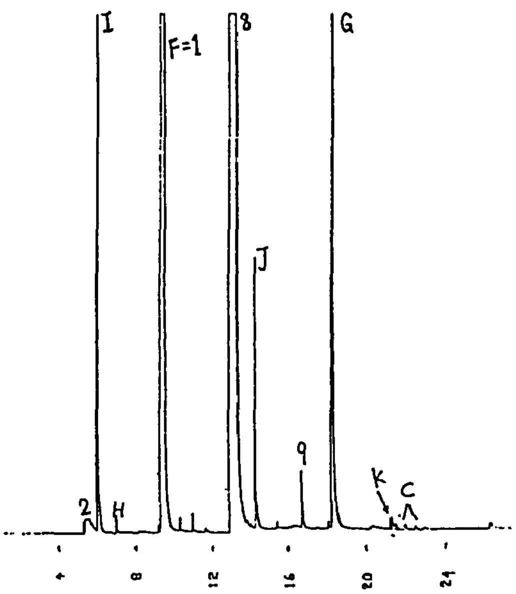


Fig. 4 The GC-spectra of radiolysis products of RSSR in ethanol (FPD). [RSSR] = 1×10^{-2} mol dm^{-3}, Dose rate = 1.2 Gy s^{-1} Absorbed dose = 16.000 Gy

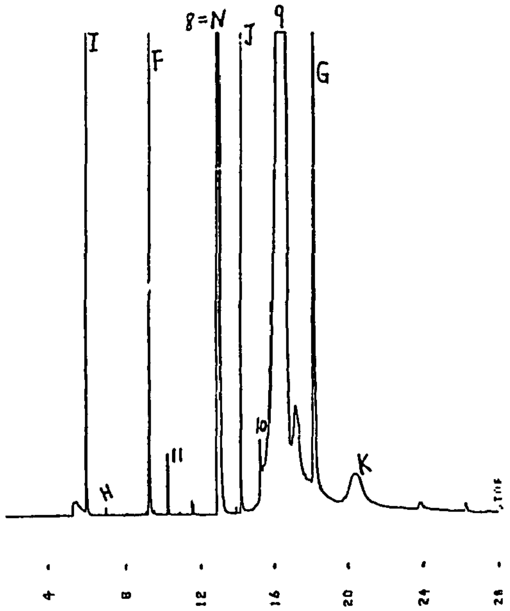


Fig. 5 The GC-spectra of radiolysis products of RSSSR in ethanol (FPD). [RSSSR] = 1×10^{-2} mol dm^{-3}, Dose rate = 1.2 Gy s^{-1} Absorbed dose = 16.000 Gy

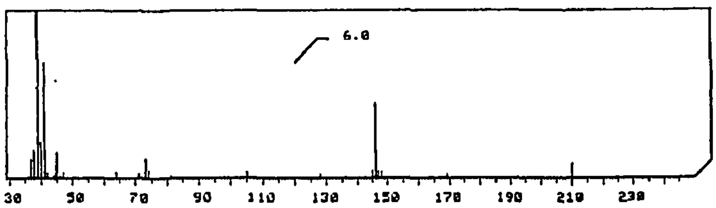


Fig. 6 The GC-MS Spectra of RSSSSR

m/e	210	169	146	136	105	73	43
Fragments	M^+	(M^+-R)	$(M-2S)^+$	($RSSS^+$-1)	RSS^+	RS^+	R^+