

## SUPPORTING INFORMATION

### **Linoleic acid peroxidation vs. isomerization: a biomimetic model of free radical reactivity in the presence of thiols**

**Branka Mihaljević,<sup>\*a</sup> Ivana Tartaro,<sup>a</sup> Carla Ferreri,<sup>\*b</sup> and Chrysostomos Chatgililoglu<sup>b</sup>**

**Materials:** Linoleic acid (>99% pure), non-ionic surfactant polyoxyethylenesorbitan monolaureate (TWEEN<sup>®</sup>-20), and 2-mercaptoethanol (2-ME), were purchased from Sigma-Aldrich. Sodium dihydrogen phosphate ( $\geq 98\%$ ) obtained from Carlo Erba, ferrous sulphate ( $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ ) and potassium thiocyanate (KSCN) from Merck. These products were used as received and all other used chemicals were of analytical reagent grade purity. Water was triply distilled, first from potassium permanganate and sodium dichromate. On the basis of UV absorption all solvents used were of analytical grade purity.

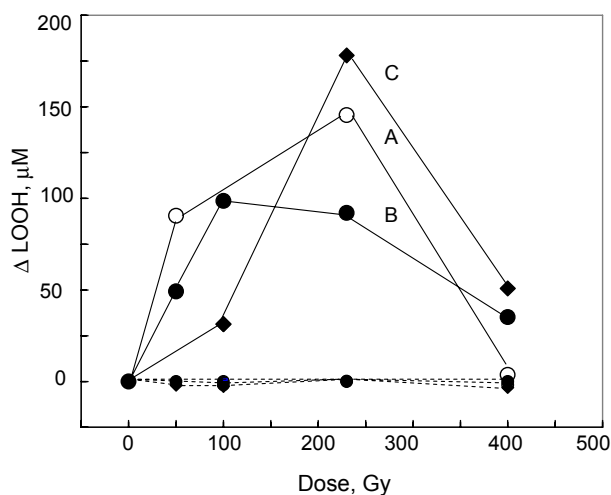


Figure S1. The formation of LOOH in micelles as a function of irradiation dose at dose rate  $1.31 \text{ Gy min}^{-1}$ ; aerobic (full lines) or anaerobic conditions (dashed lines), (○) system A (added 2-ME), (●) system B (incorporated 2-ME), (◆) control C; LH micelle:  $5 \times 10^{-4} \text{ M LH}$ ,  $2.8 \times 10^{-4} \text{ M TWEEN-20}$ ,  $5 \times 10^{-3} \text{ M PB}$  and  $2.8 \times 10^{-3} \text{ M 2-ME}$  at pH 5. Reported values represent the mean of three independent measurements ( $p < 0.05$ ); errors are  $\pm 5\%$ .

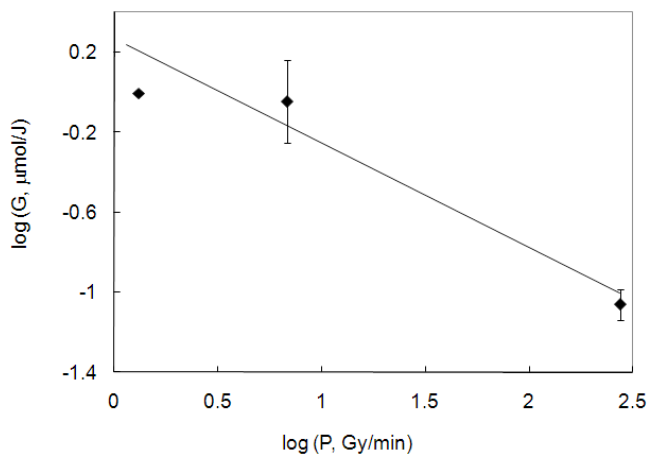


Figure S2. The effect of dose rate  $P$  on radiation-chemical yields of LOOH according to eqn (18); for experimental details see caption of Fig 2 in the main text.

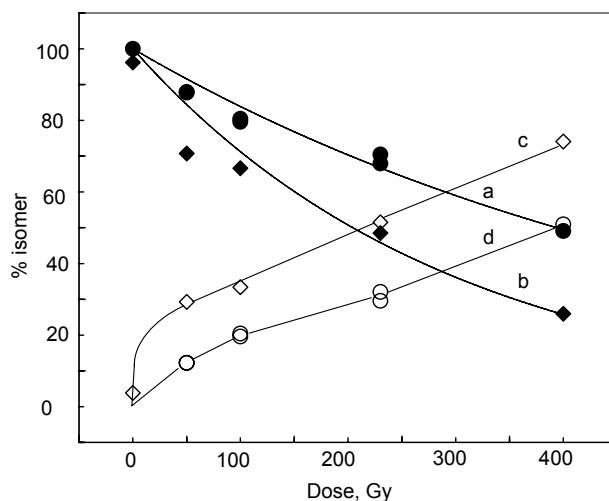


Figure S3. The influence of dose rates on geometrical isomer distribution in  $N_2O$ -saturated system B (incorporated 2-ME in micelles); The disappearance of 9c,12c-C18:2 ( $\bullet$ ,  $\blacklozenge$ ) and the formation of all-trans (mono-trans and di-trans) ( $\circ$ ,  $\diamond$ ) as a function of the irradiation dose for dose rate  $274.8 \text{ Gy min}^{-1}$  (a,d) and  $1.31 \text{ Gy min}^{-1}$  (b,c); LH micelle:  $5 \times 10^{-4} \text{ M LH}$ ,  $2.8 \times 10^{-4} \text{ M TWEEN-20}$ ,  $5 \times 10^{-3} \text{ M PB}$  and  $2.8 \times 10^{-3} \text{ M 2-ME}$  at pH 5.

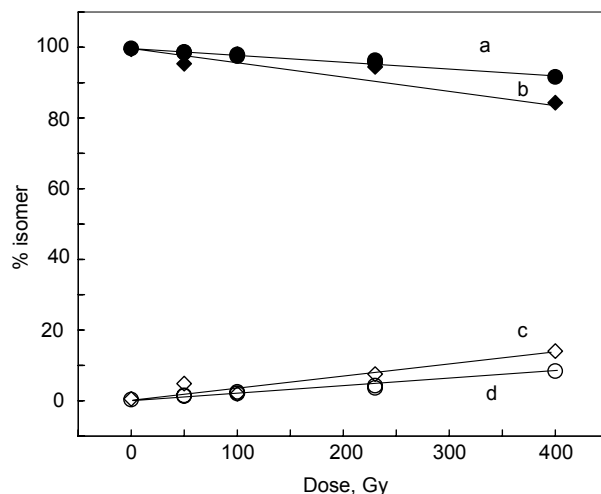


Figure S4. The influence of dose rates on geometrical isomer distribution in air-equilibrated system B (incorporated 2-ME in micelles); The disappearance of 9c,12c-C18:2 (●, ◆) and the formation of all-trans (mono-trans and di-trans) (○, ◇) as a function of the irradiation dose for dose rate  $274.8 \text{ Gy min}^{-1}$  (a,d) and  $1.31 \text{ Gy min}^{-1}$  (b,c); LH micelle:  $5 \times 10^{-4} \text{ M LH}$ ,  $2.8 \times 10^{-4} \text{ M TWEEN-20}$ ,  $5 \times 10^{-3} \text{ M PB}$  and  $2.8 \times 10^{-3} \text{ M 2-ME}$  at pH 5.

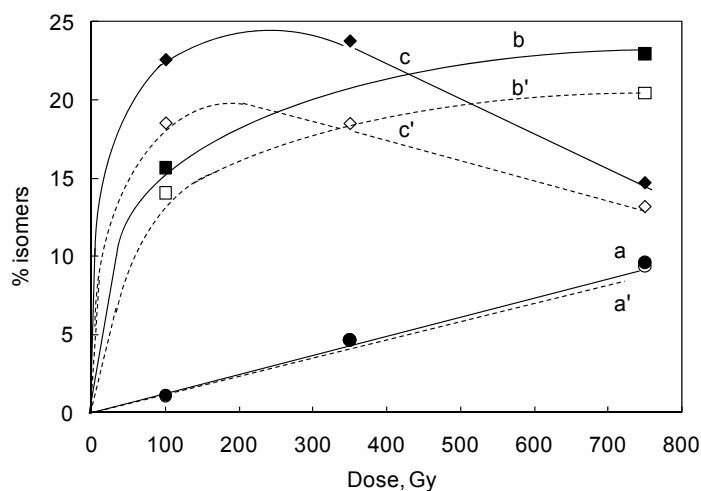


Figure S5. The influence of dose on the formation of the two mono-trans isomers 9c,12t-C18:2 and 9t,12c-C18:2, in System A under anaerobic conditions: (a) 9c,12t ( $d = 92.2 \text{ nm}$ ), (a') 9t,12c ( $d = 92.2 \text{ nm}$ ), (b) 9c,12t ( $d = 22.5 \text{ nm}$ ), (b') 9t,12c ( $d = 22.5 \text{ nm}$ ), (c) 9c,12t ( $d = 9.1 \text{ nm}$ ), (c') 9t,12c ( $d = 9.1 \text{ nm}$ ),  $P = 274.8 \text{ Gy min}^{-1}$ .

Table S1. The micelle size depending on the concentrations of TWEEN-20 and LH and the effect of size on the formation of LOOH and geometrical isomers of micelles irradiated at 100 Gy in air-equilibrated or N<sub>2</sub>O-saturated conditions.<sup>[a]</sup>

entry	d <sub>0</sub> , nm	TWEEN -20, M	LH, M	AIR		N <sub>2</sub> O
				ΔLOOH	% isomers	
				μM	9c,12c/9c,12t/9t,12c/9t,12t	9c,12c/9c,12t/9t,12c/9t,12t
1	92.2±2.9	2.8×10 <sup>-4</sup>	4.8×10 <sup>-3</sup>	48.0±0.6	96.3/1.8/1.7/0.4	97.7/1.1/1.1/0.1
2	22.5±0.8	2.8×10 <sup>-4</sup>	5.0×10 <sup>-4</sup>	15.6±0.3	93.5/3.0/3.1/0.4	63.9/14.1/15.7/6.3
3	9.1±0.7	2.8×10 <sup>-3</sup>	5.0×10 <sup>-4</sup>	14.0±1.2	94.6/2.4/2.8/0.3	47.9/18.5/22.6/10.9

<sup>[a]</sup> System A (added 2-ME in micelles); dose rate = 274.8 Gy min<sup>-1</sup>; 5.0 × 10<sup>-3</sup> M PB and 2.8 × 10<sup>-3</sup> M 2-ME at pH 5.