

## A Remarkable Antioxidation Effect of Natural Phenol Derivatives on the Autoxidation of $\gamma$ -Irradiated Methyl Linoleate

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**The antioxidation effect was remarkably enhanced in the case of natural phenol derivatives (sesamol and eugenol) as compared with synthesized butylated hydroxyanisol (BHA).**

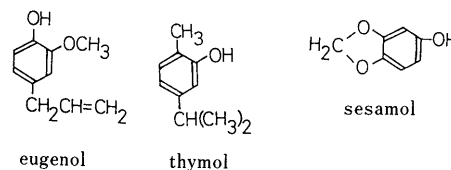
**Keywords** antioxidant;  $\gamma$ -irradiation; antioxidation; sesamol; eugenol; *G* value; methyl linoleate

Antioxidants have recently attracted considerable attention in connection with aging and the development of food additives. Various antioxidants may act as efficient free-radical scavengers and repair agents of specific-free radical damage to biomolecules. It is well known that  $\alpha$ -tocopherol is a typical example of natural antioxidants, and is not so effective as compared with synthetic antioxidants (butylated hydroxyanisol: BHA and butylated hydroxytoluene: BHT). On the other hand, sesamol is known to be an efficient antioxidant.<sup>1)</sup> Furthermore, antioxidation mechanisms and kinetics have been discussed by many researchers.<sup>2-4)</sup>

In this paper, we wish to report the antioxidation effect of natural phenol derivatives on the autoxidation of  $\gamma$ -irradiated methyl linoleate. The degree of oxidation can be generally evaluated by using the peroxidation value (*POV*). In this study, *G* values were also employed in order to evaluate the effects of various antioxidants in addition to their *POVs*. The *G* value is estimated from gas chromatograph data as described previously<sup>5,6)</sup> and reflects the degree of molecular consumption<sup>7)</sup> of methyl linoleate which might be related to peroxidation, bridging, polymerization and decomposition caused by  $\gamma$ -irradiation.

Firstly, the concentration dependence of eugenol, sesamol, and thymol on the *POVs* and *G* values for the

autoxidation of  $\gamma$ -irradiated methyl linoleate is shown in Fig. 1. The noteworthy aspects are as follows: (a) The profiles of the *POV* against the concentration of antioxidants were in good harmony with those of the *G* value. This implies that the oxidation might be connected with some structural change in methyl linoleate. (b) The *POVs* and *G* values of eugenol and thymol gradually decrease as the concentration is increased; especially, the *POV* of sesamol decreases sharply in the region of 0.1—0.2%. (c) The *POVs* and *G* values of all antioxidants employed in this study are almost constant in the high concentration region of 1.0—2.0%. (d) The *POV* increases in the order of sesamol < eugenol < thymol over the concentration range of 0.05—2.0%.



Secondly, we examined the antioxidation effect of various antioxidants including  $\alpha$ -tocopherol, flavonoids (quercetin and quercitrin), and BHA on the basis of the *POVs*, which were in proportion to the *G* values. The results are summarized in Table I. Interestingly, the *POVs* and *G* values of sesamol and eugenol were quite small as compared with those of BHA. On the other hand, no effect of quercetin and quercitrin was observed. It has already been reported that phenol derivatives having a methyl substituent at the *ortho* position of the OH group play an important role in the enhancement of antioxidation,<sup>3)</sup> and this idea might relate to the attractive results of thymol and  $\alpha$ -tocopherol in this study.

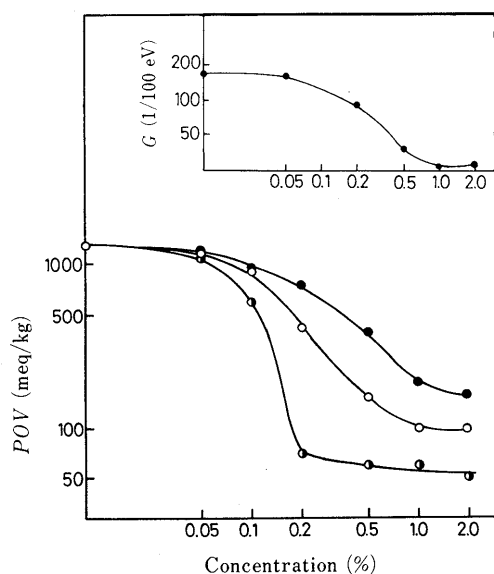
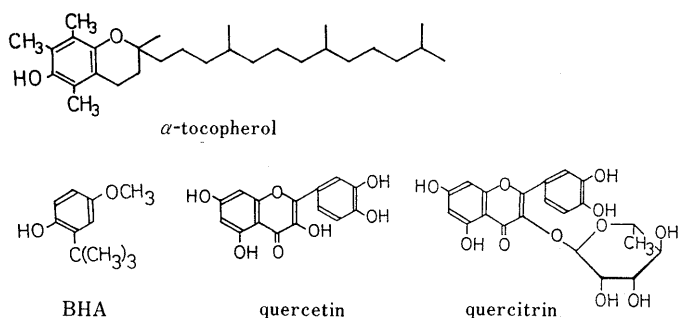


Fig. 1. The Concentration Dependence of Eugenol (○), Sesamol (●), and Thymol (●) on *POVs*, and *G* Values for the Autoxidation of  $\gamma$ -Irradiated Methyl Linoleate

TABLE I. The *POVs* and *G* Values of Various Antioxidants for the Autoxidation of  $\gamma$ -Irradiated Methyl Linoleate

Antioxidant	<i>POV</i> (meq/kg)	<i>G</i> value (1/100 eV)
—	1140	180
BHA	111	20
$\alpha$ -Tocopherol	258	35
Eugenol	109	12
Quercetin	1120	180
Quercitrin	1130	180
Sesamol	63.5	5.3
Thymol	180	27

Additive: 1% (w/w).



In conclusion, it is noteworthy that the antioxidation effect and/or the inhibitory effect of structural change in methyl linoleate was remarkably enhanced in the case of sesamol and eugenol as compared with BHA. This result suggests that sesamol and eugenol should be widely applied in medical, pharmacological, and food sciences.

#### Experimental

**Materials** Commercially available methyl linoleate (Sigma), eugenol, thymol, sesamol, quercetin, quercitrin, and BHA (Wako Chemicals) were used without further purification.

**$\gamma$ -Irradiation** Samples were irradiated with  $\gamma$ -rays (4.07 pBq- $^{60}\text{Co}$ ) for 18 h at room temperature in the atmosphere.

**Gas Chromatograph Analysis** Gas chromatography was carried out on a Yanagimoto G-3800 equipped with dual flame ionization detectors. Glass columns packed with 25% diethylene glycol succinate on 60–80 mesh Chromosorb W were used. Column temperature: 200 °C; injection temperature: 320 °C, and flow rate of carrier (He): 50 ml/min.

$G$  values are defined by using Eq. 1<sup>8)</sup>:

$$G = \frac{\text{molecular number of consumption/absorbed radiation energy of}}{100 \text{ eV}} \quad (1)$$

The  $G$  value for the autoxidation of  $\gamma$ -irradiated methyl linoleate was evaluated by using Eq. 2:

$$G = 6.023 \times 10^{23} \times 100 \times (1 - X_i/X_u) / 6.24 \times 10^{13} R \text{ M.W.} \quad (2)$$

where  $X_i$  and  $X_u$  refer, respectively, to the areas under the peak of irradiated and unirradiated methyl linoleate, and  $R$  is the dose of irradiation.

**POV Measurement** POV (meq/kg) was evaluated by use of the iodine titration method with a starch solution as an indicator.<sup>9)</sup>

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