Effect of Lipid Unsaturation on the Antioxidative Activity of Some Phenolic Acids

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Antioxidative properties of *p*-hydroxybenzoic, vanillic, syringic, 3,4-dihydroxybenzoic, *p*-coumaric, ferulic, sinapic and caffeic acids were studied in the concentration range 0.02–0.20 wt% during autoxidation at 100°C of lard and sunflower oil methyl esters (MEL and MESO, respectively). In both lipid systems, the derivatives of benzoic acid had weaker inhibiting properties than did the corresponding analogues of cinnamic acid. The effectiveness and strength of the antioxidative action were considerably lower in the lipid system MESO, which was rich in linoleic acid and was more easily oxidized. The *p*-hydroxybenzoic, vanillic, syringic and *p*-coumaric acids in this system exercised no inhibiting effect. We established that the molecules of the investigated phenolic acids initiated the chain radical process of autoxidation, and the formed antioxidant radicals propagated the chains as a result of the reaction with the lipid substrate. These reactions proceeded at a higher rate in MESO than in MEL.

KEY WORDS: Inhibited autoxidation, lipid unsaturation, phenolic acids.

The low oxidative stability of lipids, which can be mediated by antioxidant addition, is important to health protection and for economic reasons. The susceptibility of lipid systems to oxidation depends upon the strength of the C-H bond against attack by oxygen and/or peroxide radicals and plays a significant role in the inhibitor activity (1–6). The ability of antioxidants to inhibit lipid oxidation can also be affected by the binding of the fatty acids to the triacylglycerols (7,8).

The introduction of an inhibitor into the oxidizing system leads to a change in the mechanism of the process, and, as a result, of the process kinetics. The effect of an antioxidant depends on its participation and on the radicals formed from the latter in a series of reactions [7–14] (9–11):

$$LO_2^{\cdot} + InH \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} LOOH + In^{\cdot} \quad [7, -7]$$

$$In^{\cdot} + LO_2^{\cdot} \xrightarrow{k_8} In\text{-}OOL \quad [8]$$

$$In^{\cdot} + In^{\cdot} \xrightarrow{k_9} \text{products} \quad [9]$$

$$In^{\cdot} + LH \xrightarrow{k_{10}} InH + L^{\cdot} \quad [10]$$

$$InH + LOOH \xrightarrow{k_{11}} \text{products} \quad [11]$$

$$InH + O_2 \xrightarrow{k_{12}} In^{\cdot} + HO_2^{\cdot} \quad [12]$$

$$InOOL \xrightarrow{k_{13}} InO^{\cdot} + LO^{\cdot} \quad [13]$$

$$In^{\cdot} + O_2 \xrightarrow{k_{14}} InOO^{\cdot} \quad [14]$$

The stabilizing effect of antioxidants has been investigated frequently in natural fats and oils (12–16). The latter contain a series of microcomponents, such as antioxidants, free fatty acids, partial acylglycerols, sterols, fatty alcohols, dyes, metals, and primary and secondary autoxidation products. The results from numerous studies (17–19) have shown that these components may participate in and contribute to the autoxidation process and affect the inhibiting action of the added antioxidant. For that reason, the data available in the literature on the stabilizing effect of a specific antioxidant in the same fats and oils are often quite different.

Hydroxy derivatives of benzoic and cinnamic acids, which are widespread in the plant kingdom (20), possess inhibiting properties toward lipid autoxidation (21–24). Dihydroxy derivatives are more efficient than monohydroxy derivatives; the derivatives of cinnamic acid are more effective than those of benzoic acid; and the presence of one or two methoxy groups in the ortho position to the hydroxyl group increases the antioxidative effect (25–27).

The purpose of the present study was to evaluate the effect of the type and degree of lipid unsaturation on the inhibiting activity of antioxidants. The investigations were performed by using kinetically pure methyl esters of lard and sunflower oil (MEL and MESO, respectively), which represent models of two types of natural lipids that differ in unsaturation. The model lipid substrates were inhibited by derivatives of benzoic and cinnamic acids (Fig. 1).

The results are discussed taking into account that for MEL half of the hydroperoxides formed during the initial stage of the process are of a linoleate type and the other half of an oleate type, whereas linoleate hydroperoxides alone are formed during MESO autoxidation (28). Linoleate is ten times more readily oxidizable than is oleate (29–31), and the

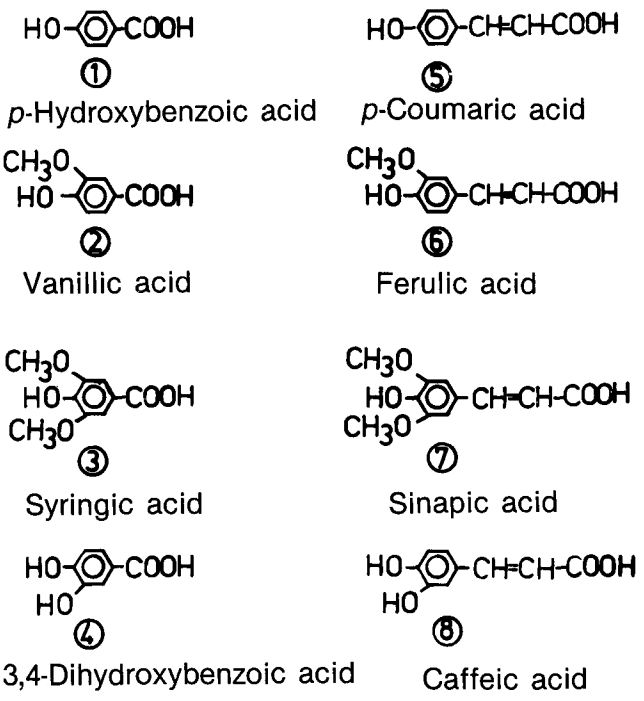

FIG. 1. Structures of the investigated phenolic acids.

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linoleate peroxide radicals are several times more reactive than are the oleate peroxide radicals (32). Oleate hydroperoxides are much more stable than are linoleate hydroperoxides (33).

EXPERIMENTAL PROCEDURES

Materials. The methyl esters of commercially available lard and sunflower oil were obtained according to Christie (34). The methyl esters were freed from pro- and antioxidants by column chromatography (35) and stored in an inert atmosphere at −20°C for no more than 10 d. The phenolics *p*-hydroxybenzoic, 3-methoxybenzoic (vanillic), 3,5-dimethoxy-4-hydroxybenzoic (syringic), 3,4-dihydroxybenzoic, 4-hydroxycinnamic (*p*-coumaric), 3-methoxy-4-hydroxycinnamic (ferulic) and 3,5-dimethoxy-4-hydroxycinnamic (sinapic) acids were from Fluka (Buchs, Switzerland), and 3,4-dihydroxycinnamic (caffeic) acid was from Merck (Darmstadt, Germany).

Gas chromatography. The fatty acid methyl esters were analyzed by using a Pye Unicam instrument, model 304, equipped with a dual flame-ionization detector and a glass capillary column (30 m × 0.2 mm i.d.) coated with SILAR 10C (Supelco Inc., Bellefonte, PA). The carrier gas was nitrogen at a flow rate of 14 mL min^{-1}. The temperature was maintained at 165°C for 5 min, then increased to 220°C at 2°C/min.

Inhibition and oxidation. Inhibition of MEL and MESO was achieved by adding aliquots of a solution of the antioxidant in purified acetone, prepared immediately before use, to a weighed lipid sample. Acetone was removed in a nitrogen (99.99%) flow. Samples containing 0.02, 0.05, 0.10 and 0.20 wt% antioxidants were prepared.

Oxidation was carried out at 100°C (±0.2°C) by blowing air through the samples (5 g) in the dark at a rate of 100 mL min^{-1}. The process was followed by withdrawing samples (*ca.* 0.1 g) at measured time intervals and subjecting them to iodometric determination of the primary product (peroxide) concentration, i.e., the peroxide value (PV) (36). The standard deviation (SD) of PV determination (in meq kg^{-1}), according to the modified iodiometric method for different mean values of PV, was (36): $\overline{PV}$ = 11.7, SD = 1.1; $\overline{PV}$ = 33.2, SD = 1.5; $\overline{PV}$ = 70.7, SD = 5.0; $\overline{PV}$ = 155.3, SD = 14.0; $\overline{PV}$ = 405.3, SD = 15.3. During the initial stage of the process, the rate of peroxide accumulation was equal to the oxidation rate (37). Kinetic curves of peroxide accumulation were plotted. All kinetic curves are the mean result of three independent experiments.

The effectiveness of the antioxidants was estimated on the basis of the induction period (IP), which was determined by the method of tangents to the two parts of the kinetic curve (38,39). Statistical analysis of IP determination (eight independent experiments) was carried out in association with previous results on inhibited oxidation (40,41) according to Doerffel (42). The SD for different mean values of $\overline{IP}$ was (in h): $\overline{IP}$ = 1.6, SD = 0.1; $\overline{IP}$ = 3.9, SD = 0.4; $\overline{IP}$ = 7.7, SD = 0.5; $\overline{IP}$ = 14.3, SD = 1.0; $\overline{IP}$ = 30.3, SD = 2.5; $\overline{IP}$ = 60.9, SD = 3.8; $\overline{IP}$ = 122.1, SD = 4.9.

The rate of noninhibited (W_0) and inhibited (W_{inh}) oxidation was determined from the tangent to the initial phase of the kinetic curves of peroxide accumulation and was expressed as mol l^{-1} s^{-1}. Recalculation of the rate from meq kg^{-1} h^{-1} into mol l^{-1} s^{-1} was performed according to the following formula:

$$1 \text{ meq kg}^{-1} \text{ h}^{-1} = 1.4 \times 10^{-7} \text{ mol l}^{-1}\text{s}^{-1} \quad [1]$$

The uninhibited and inhibited rates of autoxidation were quite constant, varying by less than 2.0%.

RESULTS AND DISCUSSION

The fatty acid compositions of MEL and MESO are shown in Table 1.

The inhibitory action is described by two kinetic characteristics (27): (i) effectiveness, representing the possibility of blocking the radical chain process by interaction with the peroxide radicals (Reaction 7), which is responsible for the duration of the IP, and (ii) strength, expressing the possibility for the inhibitor moieties to participate in other reactions, which lead to a change in oxidation rate during the IP. A measure of the effectiveness is the stabilization factor F:

$$F = IP_{inh}/IP_0 \quad [2]$$

where IP_{inh} is the induction period in the presence of an inhibitor, and IP_0 is the induction period of the noninhibited system.

The oxidation rate ratio (ORR) is a measure of the strength:

$$ORR = W_{inh}/W_0 \quad [3]$$

where W_{inh} is the oxidation rate in the presence of an inhibitor, and W_0 is the initial oxidation rate of the noninhibited system.

When ORR is larger than one, the oxidation proceeds faster in the presence of an inhibitor than in its absence, which is observed at high tocopherol concentrations (43). The lower the ORR, the stronger the inhibitor.

Figures 2 and 3 illustrate the kinetic curves of peroxide accumulation during the oxidation of MEL and MESO, respectively, in the presence of 0.05 wt% of antioxidants at 100°C. The kinetic curves of oxidation of noninhibited lipid substrates also are presented. The kinetic results for all investigated concentrations of the phenolic acids are given in Tables 2 and 3. The effectiveness and strength of the inhibitors were much lower in MESO. The easier oxidation of MESO and the higher activity of the peroxide radicals ($LO_2^{\cdot}$) formed in it are the reasons for the higher stationary concentration of

TABLE 1

Fatty Acid Composition of Methyl Esters of Lard (MEL) and Methyl Esters of Sunflower Oil (MESO) (% wt of total)[a]

Sample	14:0	16:0	16:1	18:0	18:1	18:2
MEL	2	25	22	14	48	9
MESO	—	6	—	4	24	66

[a]Triplicate values for methyl esters in standard mixture by gas chromatographic analysis varied within 12% for minor components (<5%) and within 5% for others.

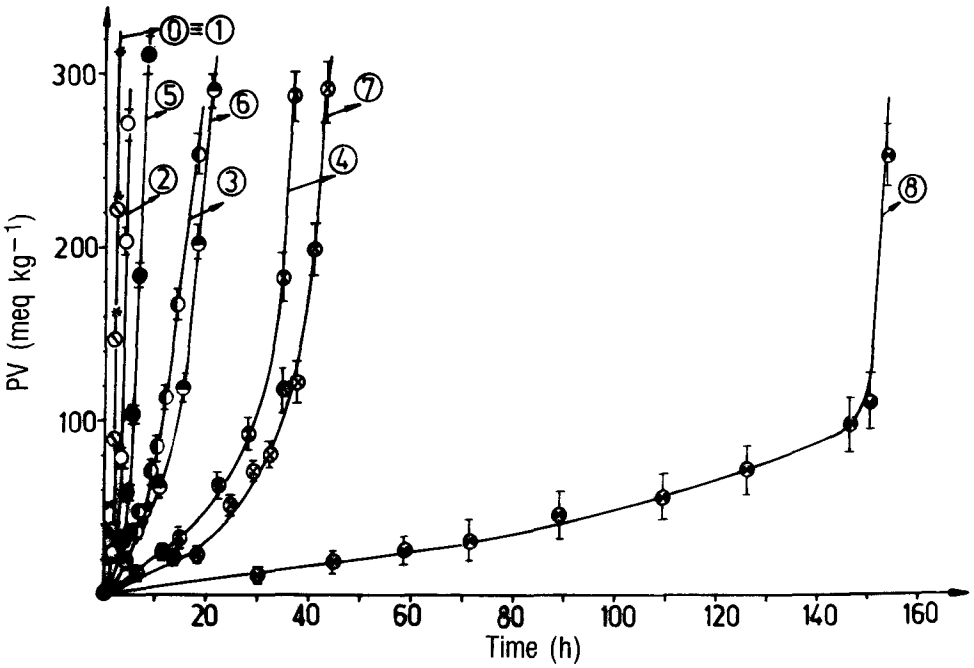

FIG. 2. Kinetic curves of peroxide value (PV) accumulation during the oxidation of methyl esters of lard at 100°C in the presence of 0.05% phenolic acids: (0) without additive, (1) *p*-hydroxybenzoic acid, (2) vanillic acid, (3) syringic acid, (4) 3,4-dihydroxybenzoic acid, (5) *p*-coumaric acid, (6) ferulic acid, (7) sinapic acid, (8) caffeic acid.

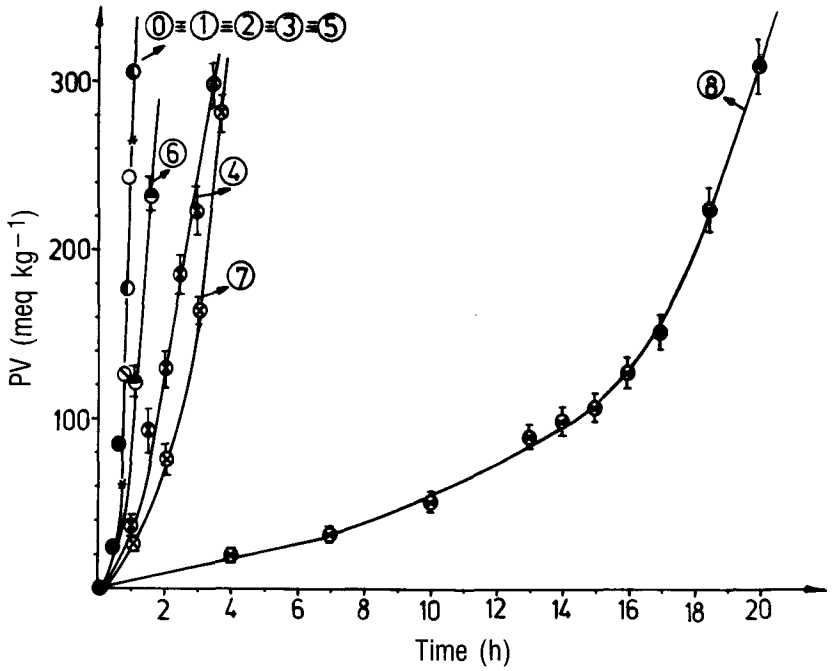

FIG. 3. Kinetic curves of peroxide value (PV) accumulation during the oxidation of methyl esters of sunflower oil at 100°C in the presence of 0.05% phenolic acids. Symbols as in Figure 2.

$LO_2^{\cdot}$ in the system, thus leading to faster consumption of antioxidants in this substrate. The results obtained indicated that in MESO, *p*-hydroxybenzoic, vanillic, syringic and *p*-coumaric acids exercised no stabilizing effect, whereas syringic acid had a weak inhibitory effect on the process at the highest concentration only (0.20 wt%) (Table 3). In MEL, all phenolic acids had antioxidant activity except *p*-hydroxybenzoic acid.

After processing the kinetic curves, the parameters characterizing the inhibitory action were obtained (Tables

TABLE 2

Kinetic Parameters Characterizing Inhibited Oxidation of Methyl Esters of Lard (MEL) at 100°C[a]

Number	Antioxidant (phenolic acid)	Inhibitor concentration wt%	Inhibitor concentration mol $l^{-1} \times 10^4$	F[b]	W_{inh}[c] $\times 10^6$, mol l^{-1} s^{-1}	ORR[d]	$\overline{W}_{inH}$[e] $\times 10^7$, mol l^{-1} s^{-1}
2	Vanillic	0.02	11.9	1.3	2.78	1.00	8.26
		0.05	29.8	1.6	2.78	1.00	10.30
		0.10	59.5	2.0	2.14	0.77	12.70
		0.20	119.0	2.3	1.85	0.67	19.40
3	Syringic	0.02	10.1	6.4	1.07	0.38	0.40
		0.05	25.3	10.2	0.87	0.31	0.59
		0.10	50.5	12.9	0.79	0.29	0.90
		0.20	102.0	17.3	0.66	0.24	1.32
4	3,4-Dihydroxybenzoic	0.02	13.0	13.8	0.69	0.25	0.22
		0.05	32.4	25.2	0.33	0.12	0.29
		0.10	64.9	33.0	0.21	0.08	0.43
		0.20	130.0	45.2	0.11	0.04	0.63
5	*p*-Coumaric	0.02	12.2	2.5	2.31	0.83	1.69
		0.05	30.5	3.5	1.74	0.63	2.65
		0.10	61.0	4.3	1.46	0.53	3.95
		0.20	122.0	5.2	1.16	0.42	6.28
6	Ferulic	0.02	10.3	6.2	1.54	0.56	0.43
		0.05	25.3	11.8	0.93	0.33	0.48
		0.10	51.5	21.9	0.62	0.22	0.53
		0.20	103.1	30.8	0.50	0.18	0.74
7	Sinapic	0.02	8.9	13.5	0.37	0.13	0.15
		0.05	22.3	28.4	0.25	0.09	0.17
		0.10	44.6	41.2	0.20	0.07	0.24
		0.20	89.3	69.6	0.15	0.05	0.28
8	Caffeic	0.02	11.1	61.0	0.063	0.023	0.05
		0.05	27.8	116.0	0.051	0.018	0.07
		0.10	55.6	152.0	0.045	0.016	0.10
		0.20	111.1	152.0	0.041	0.015	0.20

[a]W_0: initial oxidation rate of the noninhibited lipid system. $IP_0 = 1.3$ h, $W_0 = 2.78 \times 10^{-6}$ mol $l^{-1}s^{-1}$ (acids labelled as in Fig. 1).
[b]F (stabilization factor) = IP_{inh}/IP_0 (IP_{inh}: induction period in the presence of he inhibitor, IP_0: induction period of the noninhibited substrate).
[c]W_{inh}: oxidation rate in the presence of the inhibitor.
[d]ORR (oxidation rate ratio) = W_{inn}/W_0.
[e]$\overline{W}_{inH}$: mean rate of inhibitor consumption.

TABLE 3

Kinetic Parameters Characterizing Inhibited Oxidation of Methyl Esters of Sunflower Oil (MESO) at 100°C[a]

Number	Antioxidant (phenolic acid)	Inhibitor concentration wt%	Inhibitor concentration mol $l^{-1} \times 10^4$	F[b]	W_{inh}[c] $\times 10^6$, mol l^{-1} s^{-1}	ORR[d]	$\overline{W}_{inH}$[e] $\times 10^7$, mol l^{-1} s^{-1}
3	Syringic	0.02	10.1	1.0	5.56	1.00	—
		0.05	25.3	1.0	5.56	1.00	—
		0.10	50.5	1.0	5.56	1.00	—
		0.20	101.0	1.6	5.56	1.00	—
4	3,4-Dihydroxybenzoic	0.02	13.0	2.0	5.56	1.00	7.22
		0.05	32.5	3.2	4.63	0.83	8.21
		0.10	64.9	4.8	3.97	0.71	9.49
		0.20	130.0	7.0	3.48	0.62	12.04
6	Ferulic	0.02	10.3	1.0	5.56	1.00	—
		0.05	25.3	1.7	5.56	1.00	20.40
		0.10	51.5	2.2	5.56	1.00	23.80
		0.20	103.1	3.0	5.56	1.00	28.60
7	Sinapic	0.02	8.9	3.4	5.56	1.00	2.06
		0.05	22.3	5.6	4.27	0.77	2.69
		0.10	44.6	8.8	3.47	0.62	3.18
		0.20	89.3	13.2	3.09	0.56	4.07
8	Caffeic	0.02	11.1	15.6	1.16	0.21	0.42
		0.05	27.8	33.2	0.75	0.14	0.48
		0.10	55.6	44.0	0.63	0.11	0.72
		0.20	111.1	50.0	0.63	0.11	1.26

[a]$IP_0 = 0.5$ h, $W_0 = 5.56 \times 10^{-6}$ mol $l^{-1}s^{-1}$ (acids labelled as in Fig. 1). See Table 2 for footnotes b–e.

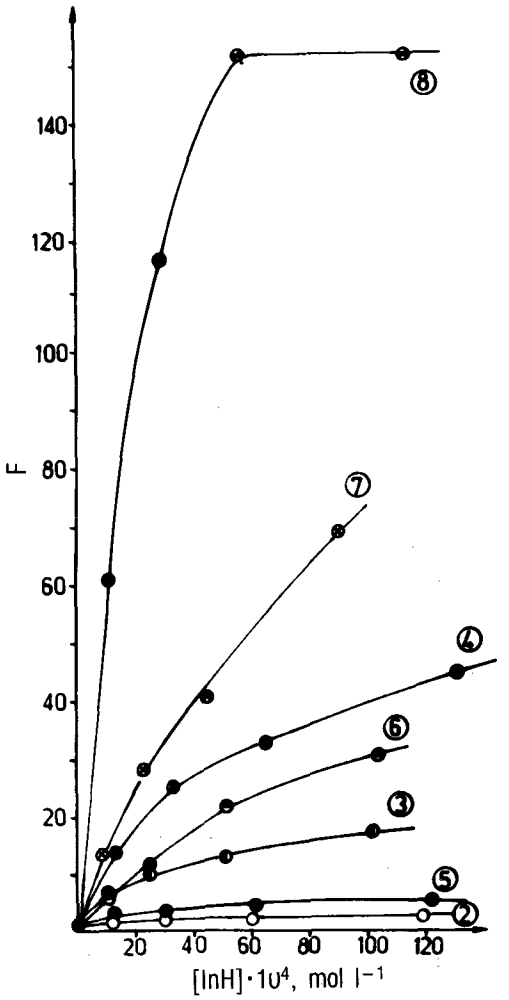

FIG. 4. Dependence of the stabilization factor F on the concentration of phenolic acids [InH]. Oxidation of methyl esters of lard at 100°C. Symbols as in Figure 2.

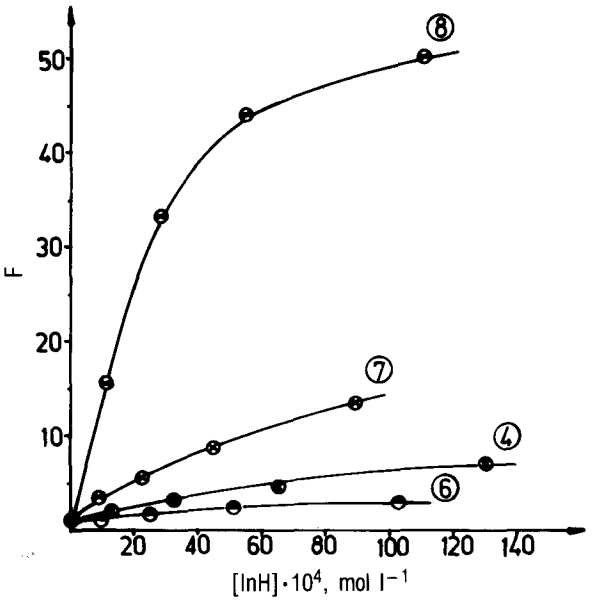

FIG. 5. Dependence of the stabilization factor F on the concentration of phenolic acids [InH]. Oxidation of methyl esters of sunflower oil at 100°C. Symbols as in Figure 2.

2 and 3). The mean rate of inhibitor consumption ($\overline{W}_{InH}$) also is given as determined according to the formula:

$$\overline{W}_{InH} = [InH]_0 / IP, \text{ mol } l^{-1}s^{-1} \quad [4]$$

where $[InH]_0$ is the initial concentration of the antioxidant (mol l^{-1}), and IP is the duration of the IP(s).

Figures 4 and 5 illustrate the dependence of the stabilization factor F on the concentration of the phenolic acids. Obviously, for all acids in MEL and MESO, respectively, these dependencies were not linear. In addition, the effectiveness of the antioxidants showing inhibitory activity in both systems increased in the sequence ferulic < 3.4-dihydroxybenzoic < sinapic < caffeic acid. The ratio between the stabilization factors of the antioxidants in MEL and MESO (F_{MEL}/F_{MESO}) changed negligibly with increased phenolic acid concentration. The data obtained also suggest that the lower the effectiveness of the inhibitor, the higher the F_{MEL}/F_{MESO} value. The F_{MEL}/F_{MESO} values, determined according to the data shown in Tables 2 and 3, ranged from 3 to 2 for the caffeic acid, from 4 to 5.3 for the sinapic acid, from 6.9 to 7.9 for the 3,4-dihydroxybenzoic acid and from 6.2 to 10.2 for the ferulic acid.

The absence of linearity of the dependencies was due to the participation of the inhibitor molecules in reactions other than the main reaction [7] of chain termination, namely reaction [11] or/and [12]. In this case there was a relationship between the mean rate of inhibitor consumption $\overline{W}_{InH}$ and the inhibitor concentration [InH] (44):

$$\overline{W}_{InH} = \overline{W}_i/f + K_{eff}[InH]^n \quad [5]$$

where $\overline{W}_i$ is the mean rate of initiation during the induction period (mol l^{-1} s^{-1}), and f is the stoichiometric coefficient of inhibition.

The results given in Tables 2 and 3 are presented as functions of the mean rates of consumption of phenolic acids $\overline{W}_{InH}$ on their concentration [InH] at different n. It was established that, for all phenolic acids with antioxidative activity in both lipid systems, this dependence was linear at n = 1 (Figs. 6 and 7), which indicated their participation in one side reaction.

The consumption of the phenolic acids, according to reaction of chain initiation [12] listed earlier, presupposes that K_{eff} should not depend on the character of the lipid medium, which was not the case (Table 4). Therefore, the phenolic acid molecules took part in the side reaction with the hydroperoxides, reaction [11]. This fact was confirmed by the different compositions and, hence, different stabilities of the MESO and MEL hydroperoxides (28), previously discussed. This information signified that the rate constants of consumption of the phenolic acids (reaction 11) would be higher in MESO than in MEL, which was proven by the K_{eff} values obtained (Table 4).

During oxidation of triacylglycerols of lard, the molecules of ferulic, sinapic and syringic acids were not

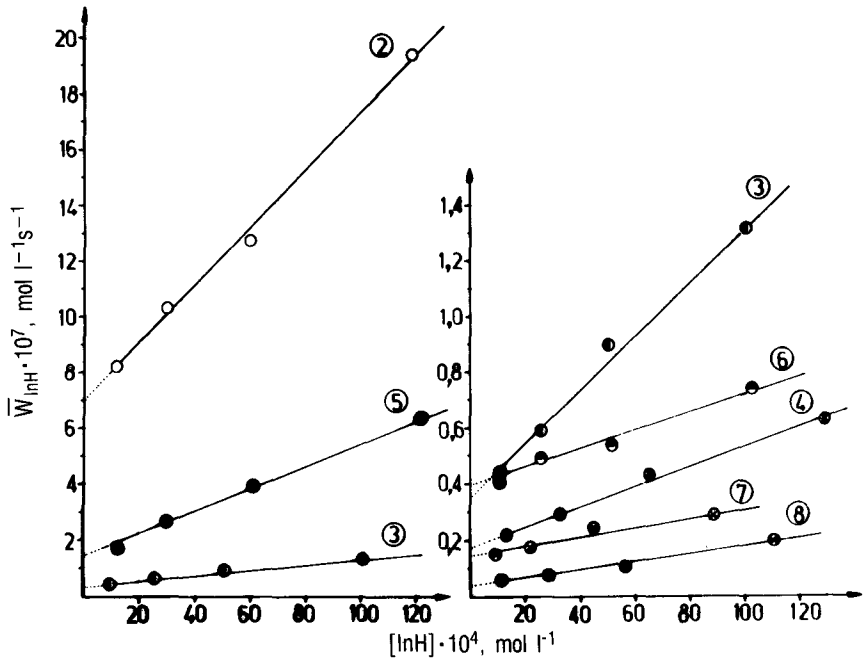

FIG. 6. Dependence of the mean rate of the consumption of phenolic acids $\overline{W}_{InH}$ on their concentration [InH]. Oxidation of methyl esters of lard at 100°C. Symbols as in Figure 2.

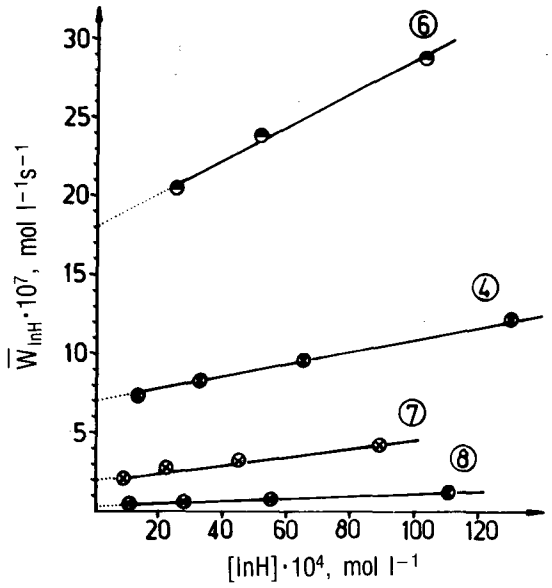

FIG. 7. Dependence of the mean rate of the consumption of phenolic acids $\overline{W}_{InH}$ on their concentration [InH]. Oxidation of methyl esters of sunflower oil at 100°C. Symbols as in Figure 2.

consumed in side reactions (41). This observation again revealed that the mechanism of inhibited lipid oxidation is affected by the binding of the fatty acids to the triacylglycerols (7,8).

Figures 8 and 9 present the dependence of the ORR on concentration of the inhibitors in MEL and MESO. Comparison of these dependencies with those concerning the stabilization factor (Figs. 4 and 5) showed that the sequence of change in the strength of phenolic acids was the same as the sequence of their effectiveness.

The oxidation rate during the IP is in a direct ratio to the rate of chain initiation and propagation. The weaker the participation of the inhibitor moieties in chain initiation and propagation, the lower the oxidation rate during the IP and the stronger the inhibitor, i.e., the lower the ORR value.

The parameter $\overline{W}_i/f$ takes into account the participation of the antioxidant in the initiation reactions. $\overline{W}_i/f$ for the inhibited systems under consideration was determined from Figures 6 and 7 by extrapolation to zero concentration of the antioxidants. The four phenolic acids (3,4-dihydroxybenzoic, ferulic, sinapic and caffeic) with antioxidant activity in the two lipid systems had a larger (2 to 30 times) increase of $\overline{W}_i/f$ in MESO than in MEL. The $\overline{W}_i/f$ was highest with the weakest antioxidant (ferulic acid), whereas it was lowest with the strongest antioxidant, i.e., the caffeic acid (see values for ORR in Tables 2 and 3 and for $\overline{W}_i/f$ in Table 4).

Previous research (9) showed that if the inhibitor radical (In$^\cdot$) participated in one reaction of a chain propagation [reaction −7 or 10 or 14], the dependence [6] was valid:

$$W_{inh} \approx [InH]^{-0.5} \quad [6]$$

When In$^\cdot$ did not participate in chain propagation, dependence [7] was valid:

$$W_{inh} \approx [InH] \quad [7]$$

Processing of the results obtained from Tables 2 and 3 on the basis of dependencies [6] and [7] showed that only dependence [6] was valid (Figs. 10 and 11). Hence, the radicals of *p*-coumaric, ferulic, syringic, 3,4-dihydroxybenzoic, sinapic and caffeic acids in MEL (Fig. 10), and of

TABLE 4

Kinetic Parameters Characterizing the Mean Rate of Initiation During the Induction Period, $\overline{W_i}/f$, and Effective Rate Constant of Inhibitor Consumption, K_{eff}[a]

Antioxidant (phenolic acid)	$\overline{W_i}/f \times 10^7$, mol $l^{-1}s^{-1}$		$K_{eff} \times 10^5 s^{-1}$	
	MEL	MESO	MEL	MESO
Vanillic	7.00	—	10.00	—
Syringic	0.39	—	1.00	—
3,4-Dihydroxybenzoic	0.17	7.0	0.38	4.20
p-Coumaric	1.40	—	4.00	—
Ferulic	0.40	18.0	0.32	10.00
Sinapic	0.15	2.0	0.16	2.40
Caffeic	0.035	0.3	0.14	0.88

[a]Temperature of oxidation was 100°C, lipid substrates were MEL and MESO. See Tables 1 and 2 for abbreviations.

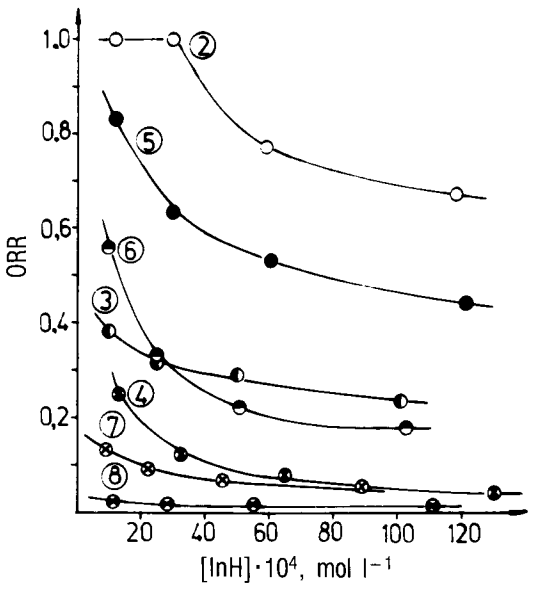

FIG. 8. Dependence of the oxidation rate ratio (ORR) on the concentration of phenolic acids [InH] during the oxidation of methyl esters of lard at 100°C. Symbols as in Figure 2.

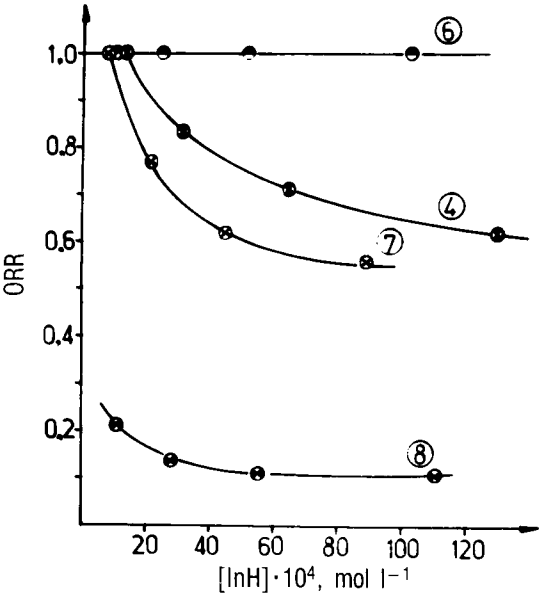

FIG. 9. Dependence of the oxidation rate ratio (ORR) on the concentration of phenolic acids [InH] during the oxidation of methyl esters of sunflower oil at 100°C. Symbols as in Figure 2.

3,4-dihydroxybenzoic, sinapic and caffeic acids in MESO (Fig. 11) participated in one reaction of chain propagation.

During the initial stage of the process, when the hydroperoxide concentration was low, the rate of reaction [−7] was negligibly low in comparison with the rate of reaction [10] (45). The strong increase of ORR during inhibited oxidation of the more easily oxidizable MESO (compare Tables 2 and 3) demonstrated the greater probability for reaction [10] and not reaction [14] to take place, because reaction [14] does not depend on the character of the substrate being oxidized. Hence, with the above inhibited systems, the only side reaction of chain propagation by the inhibitor radical was the radical interaction with the lipid substrate [10].

The data obtained also suggest that the participation of the cinnamic acid derivatives in reaction [10] is less pronounced than the participation of the benzoic acid derivatives, because, in the former case, the ORR values are lower. A probable reason for this result is the higher stability of the radicals of cinnamic acid derivatives than of the radicals formed from the benzoic acid derivatives (27).

The W_{inh} values for vanillic acid determined during the oxidation of MEL and the values for ferulic acid during oxidation of MESO showed no linear dependence on both $[InH]^{-0.5}$ and [InH], which indicated that the radicals of these phenolic acids were involved in more than one reaction of chain propagation during the oxidation of the lipid substrates.

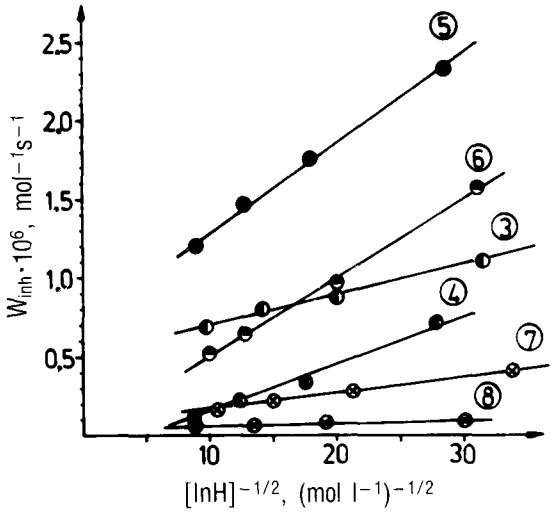

FIG. 10. Dependence of the rate of inhibited oxidation W_{inh} on the concentration of phenolic acids $[InH]^{-0.5}$ during the oxidation of methyl esters of lard at 100°C. Symbols as in Figure 2.

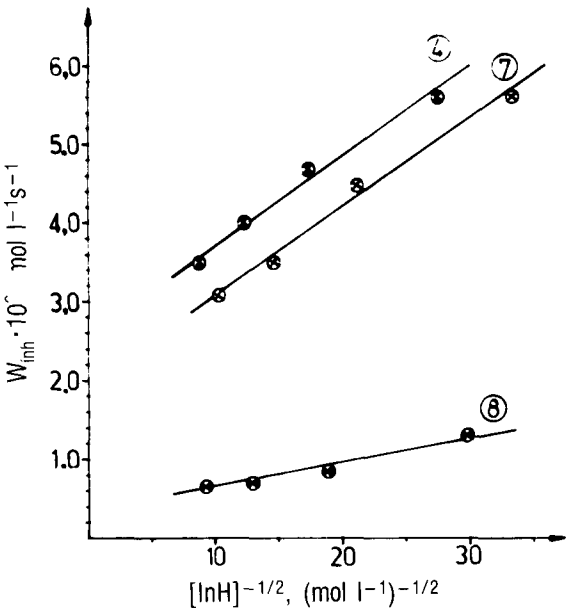

FIG. 11. Dependence of the rate of inhibited oxidation W_{inh} on the concentration of phenolic acids $[InH]^{-0.5}$ during the oxidation of methyl esters of sunflower oil at 100°C. Symbols as in Figure 2.

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