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Thermal decomposition of α-tetralyl hydroperoxide in the presence of the phenylpropionic acids

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Abstract

The thermal decomposition of cinnamic, *p*-coumaric, ferulic and sinapic acids has been investigated by employing TG/DTG/DTA methods in the temperature range at ambient to 500°C in a self-generated atmosphere. It established high thermal stability of the investigated acids. The presence of two methoxy groups in the structure increases the thermal stability of sinapic acid. The thermal decomposition of α-tetralyl hydroperoxide (THPO) in the presence of phenylpropionic acids has been investigated under nonisothermal conditions. *p*-Coumaric acid inhibited THPO thermal decomposition in the system containing 0.006, 0.018 mM acid and 0.427 mM THPO. The increased content of *p*-coumaric acid (0.049 and 0.06 mM) in the reaction system leads to rapid reaction with tetralylperoxy radicals and the formation of THPO. Cinnamic acid interacts with THPO radicals and suppresses hydroperoxide free-radical-induced decomposition. Participation of cinnamic acid is not registered in the chain–transfer reaction leading to THPO formation (investigated systems – 0.427 mM THPO and 0.006–0.06 mM cinnamic acid). Ferulic acid inhibits THPO thermal decomposition in all the mol proportions studied (THPO: ferulic acid 1: 0.012 to 0.180). Ferulic acid is regenerated as a result of the interaction between ferulic radicals and THPO. Low concentrations of sinapic acid inhibit THPO decomposition. © 1998 Elsevier Science B.V.

Keywords: Cinnamic acid; *p*-Coumaric acid; Ferulic acid; Sinapic acid; TG/DTG/DTA

1. Introduction

Numerous publications have appeared on various activities of phenylpropionic acids among which their antioxidant activity plays the major role [1–5].

Investigations concerning the role of these compounds in the initiation step of lipid peroxidation predominate [2,3,6]. The reactivity of phenylpropionic acids with peroxy and OH radicals was investigated [2].

In the last few years considerable interest has been observed in the reactions of phenoxy (and substituted phenoxy) radicals with hydroperoxides which, together with competing reactions, form the basis for the inhibition of autooxidation by phenolic substances [7].

Generally in publications till now two questions have been considered: (a) the effect of phenols on the radical–chain decomposition of hydroperoxides and (b) the effect of hydroperoxide 'build-up' on inhibition efficiency.

The investigations in this field till now have been carried out in isothermal conditions and in the pre-

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sence of solvents. The solvents take part in the reactions of thermal decomposition.

The thermal stability of the cinnamic, *p*-coumaric, ferulic and sinapic acids studied is of interest because of their radical scavenger properties. Such experiments have so far not been described in the literature.

The aim of the present investigation is to study the thermal decomposition of cinnamic, *p*-coumaric, ferulic and sinapic acids by TG/DTG/DTA and the influence of these acids on the thermal decomposition of α-tetralyl hydroperoxide.

2. Experimental

Tetralyl hydroperoxide (THPO) was prepared by air oxidation of tetralin [8] and used after a threefold recrystallization from petroleum ether (b.p. 30–50°C). Its purity was checked by melting point +54.6°C.

Phenylpropionic acids – cinnamic acid (Fluka, purity >99%), 4-hydroxy-cinnamic acid /*p*-coumaric acid/ (Fluka, purity >98%), 3-methoxy-4-hydroxy-cinnamic acid /ferulic acid/ (Fluka, purity >98%), 3, 5-dimethoxy-4-hydroxy-cinnamic acid /sinapic acid/ (Merk, purity >98%) – were used without further purification.

The thermal analyses were carried on Derivatograph Q-1500 (MOM, Budapest) under the following conditions: balance sensitivity, ±1 mg; reference, α-Al_2O_3; heating rate 2.5°C min^{-1}; Pt crucible with diameter of 7 mm. The TG/DTA experiments were conducted from ambient temperature up to 350°C and 500°C in a self-generated atmosphere.

The thermal analysis was interrupted at fixed temperature and the reaction mixture was investigated by TLC (thin layer chromatography). The composition of the reaction mixture of 0.061 mM *p*-coumaric acid and 0.427 mM THPO at 90°C and 130°C was analysed by TLC on Kieselgel 60 F_{254} (Merck), TLC system CH_2Cl_2:CH_3OH. Tetralol and tetralyl hydroperoxide was analyzed by TLC system *n*-hexane: $CH_3COOC_2H_5$. The composition of the reaction mixture of 0.051 mM ferulic acid and 0.427 mM THPO at 120°C was analyzed by TLC on Kieselgel 60 F_{254} (Merck), TLC system CH_2Cl_2:CH_3OH.

3. Results, discussion

The presence of –OH group and conjugated double bonds in the structure of the investigated phenylpropionic acids (cinnamic, *p*-coumaric, ferulic and sinapic acid) (Fig. 1) determine their behaviour as inhibitors.

The variations in the character of the thermal destruction of phenylpropionic acids are presented in Table 1 and Figs. 2–4. The data in Fig. 2 demonstrate a two-stage process of cinnamic acid decomposition in the 155–250°C and 250–275°C ranges. During the first step, an endothermic peak at 130°C is indicative of the phase transition (solid–liquid state).

The rest of the material after 260°C undergoes a thermal oxidative decomposition, recorded as an exothermic peak at 265°C.

As the melting of *p*-coumaric acid (the endothermic peak at 200°C) was accompanied by rapid decomposition, the TG/DTG/DTA experiment of this acid failed. The initial temperature of decomposition (T_i) is 180°C. The rapid thermal decomposition at 190–210°C could be due to the known destruction of *p*-coumaric acid to the thermal unstable coumarin and its derivatives [9].

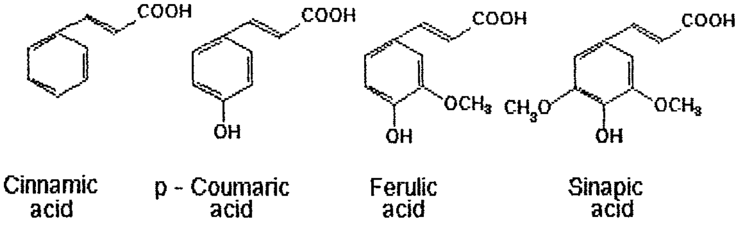


Fig. 1. Described in the manuscript.

Table 1
Thermal decomposition of phenylpropionic acids

No	Acids	Stage	Temperature interval of decomposition	Mass loss, %	$W_{max}{}^{a}$ °C	Thermal interval, °C		Residue at 500°C, %
						endo	exo	
1.	Cinnamic acid	1	155^{b}–260	90.0	250	130		
		2	260–275	8.5	265	415	265	1.5
2.	Ferulic acid	1	125^{b}–230	45.7	200	158		
		2	230–330	14.4				
			330–500	27.2				12.7
3.	Sinapic acid	1	145^{b}–240	37.2	200	195		
		2	240–325	25.6				
		3	325–500	37.2		360		0

[a] DTG maximum.
[b] T_i – an initial temperature of decomposition.

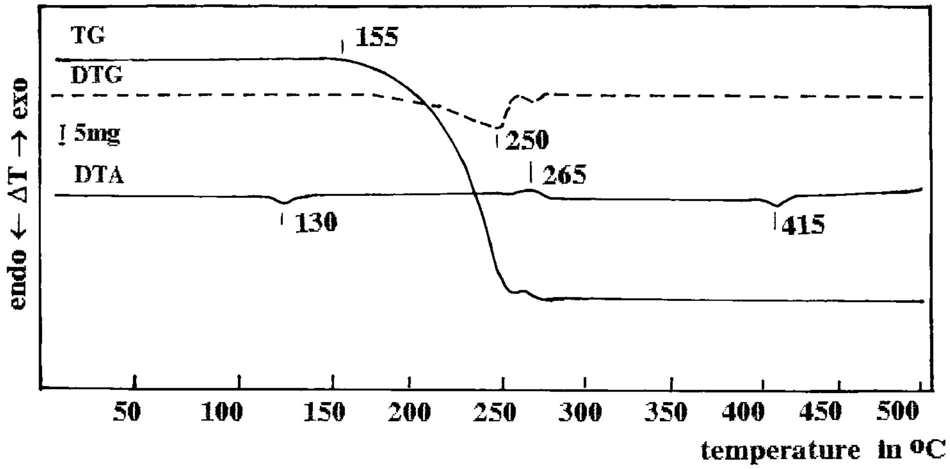


Fig. 2. Thermal decomposition of cinnamic acid.

The TG and DTG curves for ferulic acid (Fig. 3, Table 1) registered a three-step weight loss process in a temperature range 20–500°C. The melting of the sample is accompanied by evaporation and degradation – the weight loss was 1.8% at m.p. 158°C. The TG data show that T_i of ferulic acid is considerably lower than T_i of cinnamic and *p*-coumaric acids. Intensive thermal decomposition of ferulic acid occurred at a range of 125–230°C and resulted in a 45.7% weight loss.

Some products of the thermal oxidative degradation of ferulic acid have been identified as vanillin and gwaicol [10]. The 4-vanillingwaicol has been found as a result of thermal decarboxylation of ferulic acid [11]. In our investigation the DTA curve indicates lack of thermal effects due to the formation of stable intermediates.

The presence of two methoxy groups increases the thermal stability of sinapic acid. The initial temperature of the thermal decomposition is 20°C higher than that of ferulic acid (Table 1). The endothermic peak at 195°C registered the melting of the sample (Fig. 4). The thermal decomposition of sinapic acid proceeds as a three-stage reaction. The TG/DTA data show that sinapic acid undergoes an intensive destruction at the 145–240°C range, resulting in the formation of thermally stable products. The last were decomposed at the 240–500°C range.

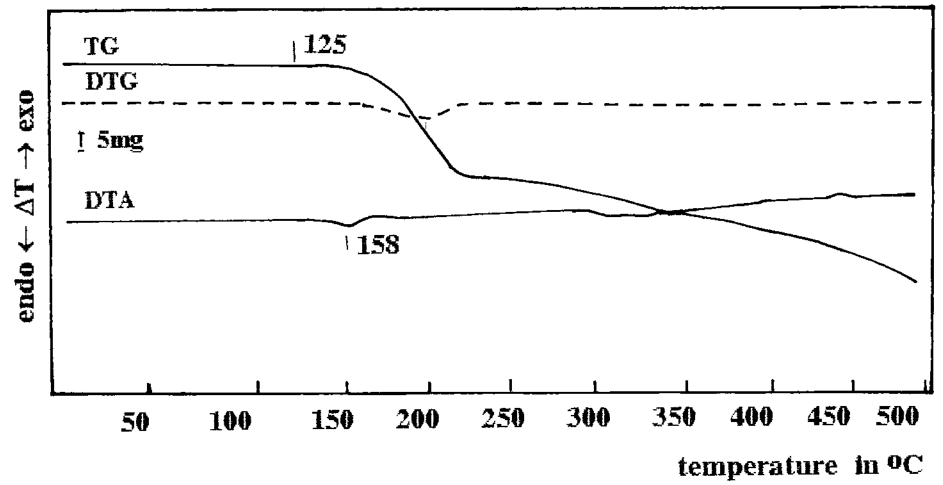


Fig. 3. Thermal decomposition of ferulic acid.

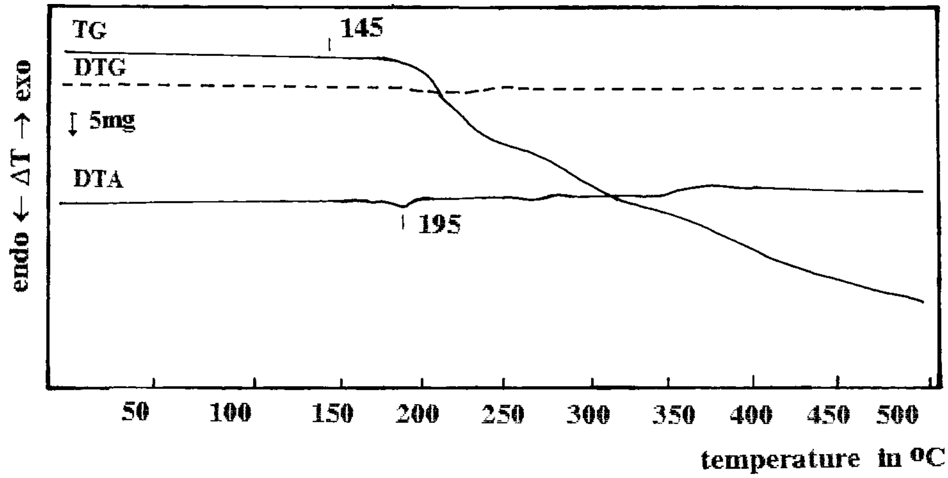


Fig. 4. Thermal decomposition of sinapic acid.

The TG/DTG/DTA data show high thermal stability of the investigated phenylpropionic acid.

The study on their inhibitory properties by TG/DTA requires a thermally stable generator of the radical. In our study we used the thermally stable α-tetralinhydroperoxide as a generator of the tetraloxy-, peroxy- and hydroxy-radicals:

$$\mathrm{TOOH} \rightarrow \mathrm{TO}^\circ + {}^\circ\mathrm{OH} \quad (1)$$

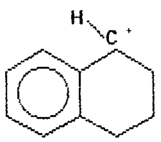
$$\mathrm{TOOH} + \mathrm{TOOH} \rightarrow \mathrm{TO}_2^\circ + \mathrm{TO}^\circ + \mathrm{H_2O} \quad (2)$$

where T is

$$\mathrm{TOOH} \rightarrow \mathrm{TO}^\circ + {}^\circ\mathrm{OH}$$

$$\mathrm{TOOH} + \mathrm{TOOH} \rightarrow \mathrm{TO}_2^\circ + \mathrm{TO}^\circ + \mathrm{H_2O}$$

where T is



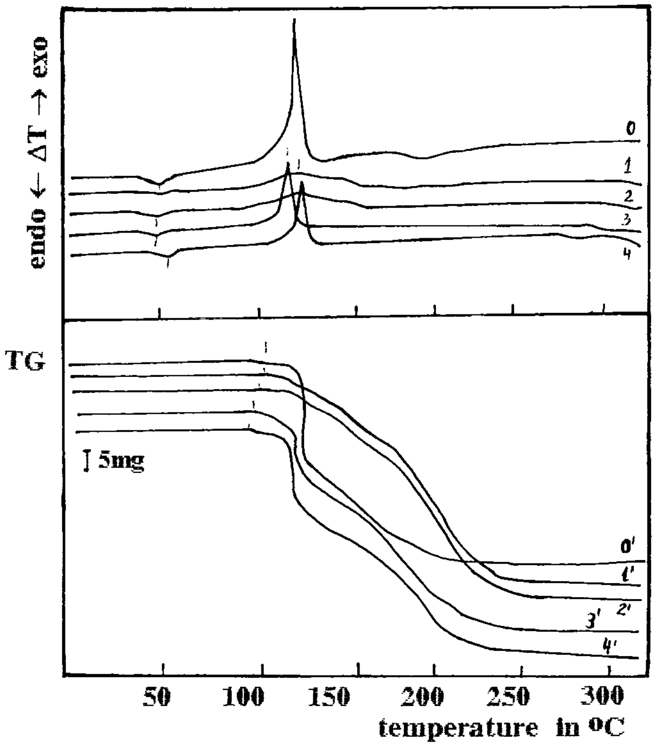


Fig. 5. Thermal decomposition of the α-tetralylhydroperoxide in the presence of the p-coumaric acid: 0,0′–0.427 mM THPO; 1,1′–0.427 mM THPO and 0.006 mM p-coumaric acid; 2,2′–0.427 mM THPO and 0.018 mM; p-coumaric acid; 3,3′–0.427 mM THPO and 0.049 mM p-coumaric acid; 4,4′–0.427 mM THPO and 0.061 mM p-coumaric acid.

In a previous study [12] a two-stage decomposition of α-tetralyl hydroperoxide has been established during its thermochemical degradation under nonisothermal conditions without solvents. The thermal decomposition of THPO during the temperature interval 105–165°C proceeds both as thermal homolysis and free-radical-induced decomposition. The phenylpropionic acids as radical scavengers could inhibit the free-radical-induced decomposition of the hydroperoxide and terminate the radical–chain reactions.

The TG/DTA data of the THPO decomposition in the presence of p-coumaric acid show a similar two-stage decomposition (Fig. 5, Table 2). The effect of p-coumaric acid on THPO decomposition is demonstrated most distinctly by the DTA data during the first stage (Fig. 5). The height of the exothermic peak which corresponds to the thermal effect of interaction between THPO radicals and p-coumaric acid decreases significantly compared to that of the neat THPO (Fig. 5, curves 0 and 1, 2,3,4).

The TG data of THPO decomposition in the presence of the 0.006 mM p-coumaric acid (Fig. 5, curve 1′) show a weight loss of only 4% during the first stage of decomposition while the weight loss of the neat THPO is 30% in the same temperature range (Table 2). The increase of p-coumaric acid (0.018 mM) in the reaction system leads to a decrease of the enthalpy changes in the 105–145°C range (Fig. 5, curves 0,1 and 2). The temperature maximum of the exothermic peak presenting the enthalpy changes of interaction between the THPO radicals and 0.018 mM p-coumaric acid is shifted to a higher temperature compared to the maximum of the system containing 0.006 mM p-coumaric acid (Table 2, Nos. 1 and 2).

The reaction scheme of that interaction can be demonstrated by the equations:

$$TO^{\circ} + AH \rightarrow TOH + A^{\circ} \qquad (3)$$

$$TO_2^{\circ} + AH \rightarrow TOOH + A^{\circ} \qquad (4)$$

Table 2
Thermal decomposition of α-tetralyl hydroperoxide in the presence of *p*-coumaric acid

No	Products/mM	Stage	Temperature ranges of decomposition	Mass loss,%	W_{max}[a], °C	Thermal effects, °C	
						endo	exo
0	0.427 THPO	1	105[b]–165	30.0	165	54	160
		2	165–250				
1.	0.427 THPO and 0.006 *p*-coumaric acid	1	105[b]–135	4.0	135	50	135
		2	165–280	87.7	210		
2.	0.427 THPO and 0.018 *p*-coumaric acid	1	105[b]–145	6.8	145	50	145
		2	145–300	78.1	215		
3.	0.427 THPO and 0.049 *p*-coumaric acid	1	100[b]–140	19.0	140	50	140
		2	140–300	58.0	180		
4.	0.427 THPO and 0.061 *p*-coumaric acid	1	100[b]–150	23.7	150	52	145
		2	150–305	57.0	190		

[a] DTG maximum.

[b] T_i – an initial temperature of decomposition.

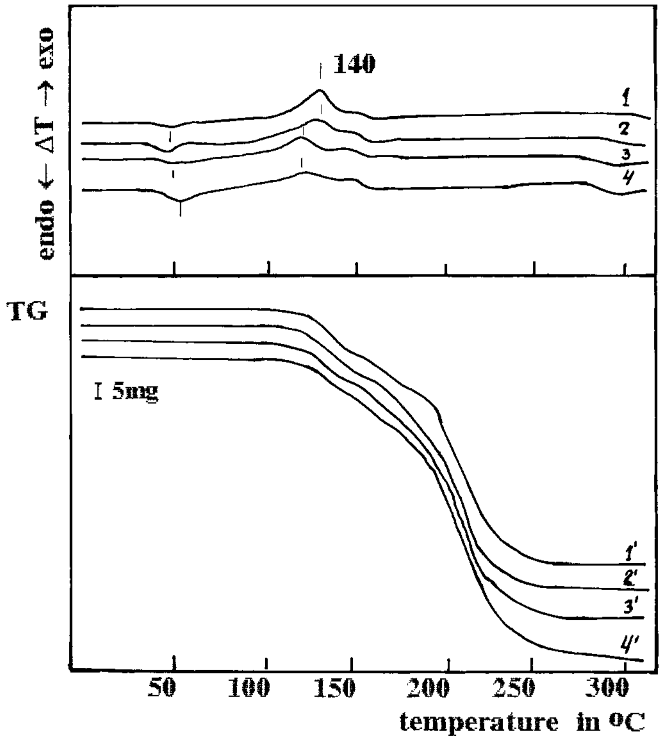


Fig. 6. Thermal decomposition of the α-tetralylhydroperoxide in the presence of the cinnamic acid: 1,1′–0.427 mM THPO and 0.007 mM cinnamic acid; 2,2′–0.427 mM THPO and 0.020 mM cinnamic acid; 3,3′–0.427 mM THPO and 0.054 mM cinnamic acid; 4,4″–0.427 mM THPO and 0.068 mM cinnamic acid.

$$A^\circ + \mathrm{TOOH} \rightarrow \mathrm{AH} + \mathrm{TO}_2^\circ \qquad (5)$$

$$A^\circ + \mathrm{TO}_2^\circ \rightarrow \mathrm{TOOA} \qquad (6)$$

$$A^\circ + {}^\circ A \rightarrow A - A \qquad (7)$$

where AH is *p*-coumaric acid.

In the scheme presented we do not describe the $^\circ$OH scavenging activity of *p*-coumaric acid since the rate constant of the reaction is low at low acid concentration [2].

The TG/DTA data of the system, containing 0.049 and 0.061 mM *p*-coumaric acid and 0.427 mM THPO (Fig. 5, curves 3 and 4) confirmed the reaction mechanism. The increase of *p*-coumaric acid facilitates THPO homolysis as a result of its interaction with TO$^\circ$ and $^\circ$OH radicals. The DTA curves of the systems containing 0.049 and 0.061 mM *p*-coumaric acid registered an intensive exothermic reaction at 140°C and 145°C due to rapid radical decomposition (Fig. 5, curves 3 and 4). However, the weight loss is lower than that observed during the THPO free-radical-induced decomposition of neat THPO (Table 2). The results suggest that THPO formed by reaction (4) is responsible for the rapid radical decomposition (Fig. 5, curves 3 and 4). We investigated the products of thermochemical changes of system, containing 0.061 mM *p*-coumaric acid and 0.427 mM THPO at 90°C by TLC. The observed THPO and traces of tetralol in TLC of the reaction mixture at 90°C are result of reactions (3) and (4). The presence of *p*-coumaric acid and absence of THPO were established by TLC in the reaction mixture at 130°C. The presence of *p*-coumaric acid gives us a reason not to ignore the interaction between *p*-coumaryl radicals and THPO (reaction 5).

p-Coumaric acid inhibited THPO thermal decomposition in mol proportions THPO:*p*-coumaric acid 1: 0.014 to 0.042.

TG/DTA data of the systems containing THPO and cinnamic acid surprisingly showed cinnamic acid suppressing THPO radical decomposition (Fig. 6). Independently of the absence of the OH group in the structure, cinnamic acid interacts with radicals resulting from tetralylhydroperoxide decomposition. The temperature maximum of the exothermic peak, presenting the enthalpy changes of interaction between THPO radicals and 0.054 and 0.068 mM cinnamic acid is shifted to a lower temperature compared to the maximum of the system containing 0.007 mM and 0.02 mM cinnamic acid (Fig. 6, curves 1, 2, 3 and 4, Table 3). The rapid radical reaction – indicative for THPO free-radical-induced decomposition – was not observed on DTA curves of a system with cinnamic acid.

The results published till now indicate [6] that the peroxy value insignificantly decrease in lipid substrates, containing cinnamic acid. Most probably cinnamic acid does not take place in chain–transfer

Table 3
Thermal decomposition of α-tetralyl hydroperoxide in the presence of cinnamic acid

No	Products/mM	Stage	Temperature ranges of decomposition	Mass loss,%	W_{max}[a], °C	Thermal effect,°C	
						endo	exo
1.	0.506 THPO and 0.007 cinnamic acid	1	105[b]–145	11.9	140	50	140
		2	145–165	20.2	160		
		3	165–270	55.0	220		
2.	0.506 THPO and 0.020 cinnamic acid	1	105[b]–150	10.5	140	50	140
		2	150–170	8.1	160		
		3	170–260	63.9	210		
3.	0.506 THPO and 0.054 cinnamic acid	1	105[b]–140	6.5	130	50	130
		2	140–260	8.7	150		
		3	160–260	74.7	210		
4.	0.506 THPO and 0.068 cinnamic acid	1	100[b]–160	16.0	130	55	130
		2	160–270	74.5	210		

[a] DTG maximum.

[b] T_i – an initial temperature of decomposition.

Table 4
Thermal decomposition of α-tetralyl hydroperoxide in the presence of ferulic and sinapic acids

No	Products/mM	Stage	Temperature ranges of decomposition	Mass loss,%	W_{max}[c], °C	Thermal effect, °C	
						endo	exo
1.	0.427 THPO and 0.005 ferulic acid	1	105[b]–140	9.8	130	50	140
		2	140–270	74.6	200		
2.	0.427 THPO and 0.015, 0.031 and 0.044 ferulic acid[a]	1	95[b]–140	12.4	130	50	140
		2	140–290	76.5	190		
3.	0.427 THPO and 0.051 ferulic acid	1	90[b]–300	83.7	140 200	50	90,140
4.	0.427 THPO and 0.077 ferulic acid	1	85[b]–315	82.7	205	50	95,140
5.	0.427 THPO and 0.004 sinapic acid	1	85[b]–130	18.3	125	50	125
		2	130–250	88.7			
6.	0.427 THPO and 0.012 sinapic acid	1	100[b]–140	37.0	140	50	140
		2	140–270	72.6	260		

[a] The TG/DTG/DTA curves with 0.015, 0.031 and 0.044 mM ferulic acid are identical.
[b] T_i – an initial temperature of decomposition.
[c] DTG maximum.

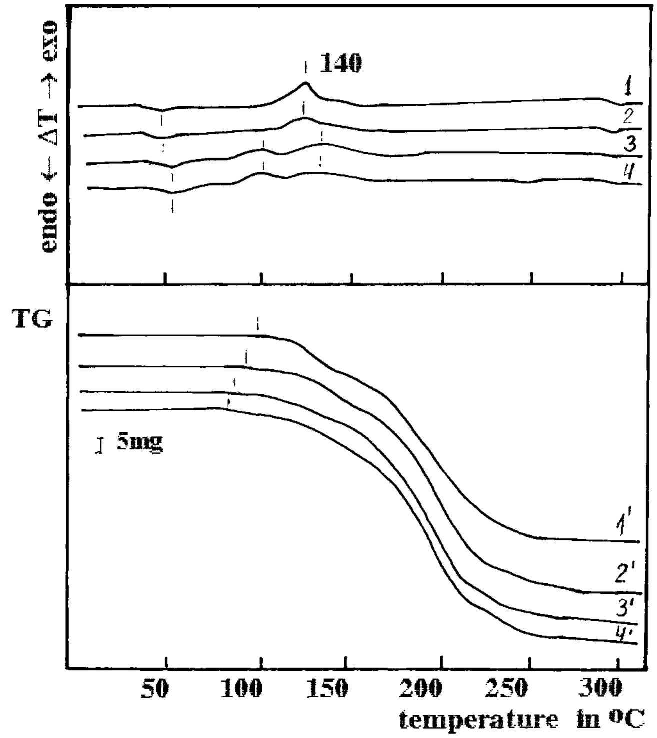
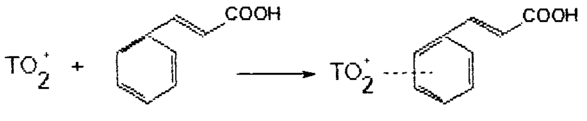


Fig. 7. Thermal decomposition of the α-tetralylhydroperoxide in the presence of the ferulic acid: 1,1′–0.427 mM THPO and 0.005 mM ferulic acid; 2,2′–0.427 mM THPO and 0.015 mM ferulic acid; 3,3′–0.427 mM THPO and 0.051 mM ferulic acid; 4,4′–0.427 mM THPO and 0.077 mM ferulic acid.

reaction (4) generating THPO. The probable reaction is:



The maximum rate of destruction at 210°C – registered from DTG curves – is indicative of the formation of thermally stable compounds as a result of interaction between the products of THPO decomposition and cinnamic acid. In conclusion, cinnamic acid participates in radical reaction and terminates THPO decomposition.

From the TG/DTA data of the systems containing THPO and ferulic acid (Table 4, Fig. 7) we observe that ferulic acid (in all investigated proportions) inhibits hydroperoxide decomposition. The rate of the thermal reaction in the systems containing 0.015, 0.031 and 0.044 mM ferulic acid does not depend on the acid's concentration. This fact is supported by identical thermal changes registered by the TG/DTA curves of these systems (Table 4, No. 2).

Recently in the literature it has been described that the lipid substrate in the presence of ferulic acid accumulates higher concentration of peroxy radicals than in the presence of the *p*-coumaric acid [6]. In our experimental conditions ferulic acid being an effective radical acceptor facilitates THPO thermal homolysis. The T_i of THPO decomposition in the presence of ferulic acid is 10–15°C lower, (Table 4, Nos. 2–4) than T_i of neat THPO (Table 2, No. 0).

In the systems containing 0.051 and 0.077 mM ferulic acid we observe the exothermic peak maximum shifted to higher temperature (Fig. 7 curves 1, 2 and 3, 4). On the DTA curves of the systems containing 0.051 and 0.077 mM ferulic acid new exothermic reaction appears in the temperature range 90–115°C. We suppose that these new enthalpy changes are a result from reaction (5), leading to the regeneration of

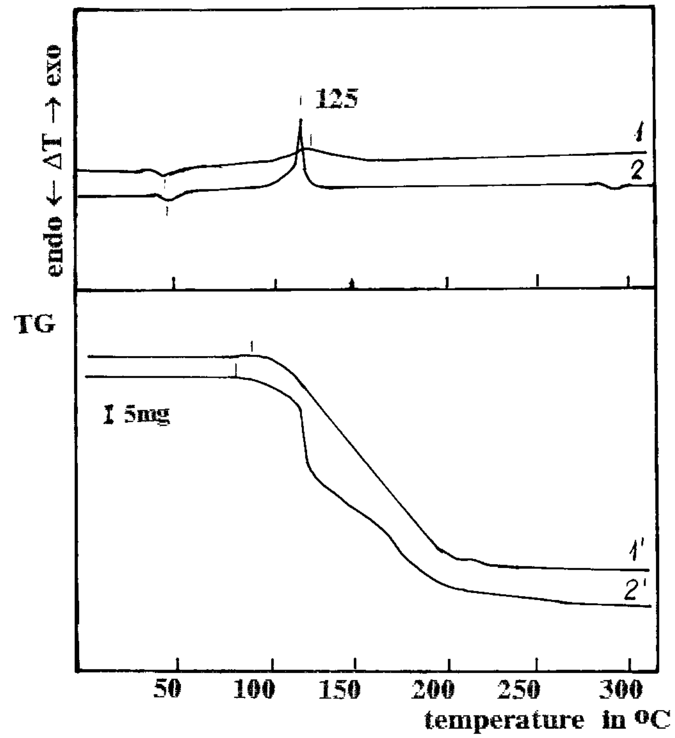


Fig. 8. Thermal decomposition of the α-tetralylhydroperoxide in the presence of the sinapic acid: 1,1′–0.427 mM THPO and 0.004 mM sinapic acid; 2,2′–0.427 mM THPO and 0.012 mM sinapic acid.

ferulic acid. The last assertion was confirmed by TLC of the reaction mixture at 120°C.

THPO decomposition in the presence of the 0.004 mM sinapic acid proceeds as thermochemical destruction without rapid free-radical-induced decomposition (Fig. 8, curves 1,1′). In the system with a higher content of sinapic acid (0.012 mM) THPO is formed as a result of reaction (4). Thermal decomposition of the newly obtained THPO is observed by DTA data – exothermic peak at 140°C (Fig. 8, curve 2). By an increase of sinapic acid in the sample to 0.05 mM the enthalpy changes in the 90–120°C temperature range, indicative for reaction (5), are not observed.

Sinapic acid is effective radical acceptor at lower concentrations.

4. Conclusions

The thermal decomposition of cinnamic, *p*-coumaric, ferulic and sinapic acids proceeds as a multi-stage process in the temperature range from ambient to 500°C. The presence of two methoxy groups in the structure increases the thermal stability of sinapic acid.

p-Coumaric acid inhibits THPO thermal decomposition in the system containing mol proportions THPO: *p*-coumaric acid 1:0.014 to 0.042. The increased content of *p*-coumaric acid in the reaction system leads to rapid reaction with tetralylperoxy radicals and the formation of THPO.

Cinnamic acid interacts with THPO radicals and suppresses hydroperoxide free-radical-induced decomposition. The participation of cinnamic acid (investigated systems – 0.506 mM THPO and 0.006 to 0.068 mM cinnamic acid) is not registered in the chain–transfer reaction leading to THPO formation.

Ferulic acid inhibits THPO thermal decomposition in all the mol proportions studied (THPO:ferulic acid 1: 0.012 to 0.18). Ferulic acid is regenerated as a result of the interaction between ferulic radicals and THPO.

Low concentrations of sinapic acid inhibit THPO decomposition.

Acknowledgements

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