

Vegetal polyphenols as antioxidants in polymers

S. JIPA^{a,b,*}, T. ZAHARESCU^a, W. KAPPEL^a, T. SETNESCU^{a,b}, M. LUNGULESCU^a, R. OLTEANU^b

^aNCDE ICPE CA, 313 Splaiul Unirii, P. O. Box 149, Bucharest 030138, Romania

^b“Valachia” University of Targoviste, 18-22 Unirii Av., Targoviste 130082, Romania

Flavonoids, such as quercetin, kaempferol, apigenin, myricetin, luteolin, are a group of polyphenolic compounds, which naturally exist (e. g. in plants of Apiaceae family) and serve as antioxidants in vegetables. The inhibition in the oxidation of paraffin occurred in air due to four different plant extracts (parsley, dill, celery and lovage) was investigated using the isothermal chemiluminescence method. All samples showed marked antioxidant activity at the concentration of 0.25 % w/w. The results suggested that radical trapping effects of flavonoids differ according to their structure

(Received February 25, 2008; accepted April 2, 2008)

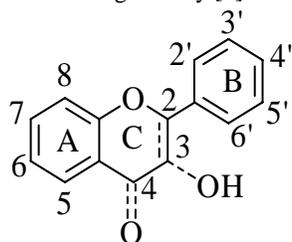
Keywords: Flavonoids, Plant extracts, Chemiluminescence, Peroxy radical scavenging

1. Introduction

Thermal stability of polymeric materials for packaging is an important physico-chemical property which can restrict or enlarge the application areas of materials. The material behavior may be profoundly modified by the addition of compounds acting as antioxidants. Lots of these compounds were found to be carcinogenic or toxic, and therefore must be excluded from the polymer usage in packaging food industry. Optimization of the packaging material and additives with respect to toxicity and migration in food represents a relevant key of the appropriate strategy.

Vegetables are a good source of natural antioxidants, containing many different flavonoids which can provide protection against thermal degradation of packaging material.

Flavonoids are a group of natural benzo- γ -pyrone derivatives having a good free-radical scavenging activity [1-3] or metal-chelating activity [4].



Three structural groups are important determinants for radical-scavenging activity: the ortho-dihydroxy structure in the B-ring, as well as the 2,3 double bond in conjugation with a 4-oxo function in the C-ring. Flavonoids form binding complexes with metal ions by the 3- or 5-hydroxyl- and 4-ketosubstituents or hydroxyl groups in ortho position in B-ring.

The aim of this study was to determine the inhibition in the oxidation of paraffin occurred in air due to four different plant extracts (parsley, dill, lovage and celery) using the isothermal chemiluminescence method.

2. Experimental

The analyzed dry species were: *Petroselinum Crispum* (parsley), *Anethum Graveolens* (dill), *Levisticum Officinale* (lovage) and *Apium Graveolens* (celery). The samples were ground and homogenized immediately before maceration.

The dried plants (10 g) and the extracting solvent (ethanol) were placed in an Erlenmeyer flask (250 mL); the ratio of plant material and extracting solvent was 1:10 w/v. Maceration was performed for 120 hours at room temperature.

The liquid extract was separated from the plant material by filtration, the solvent was evaporated under vacuum, and the dry extract was used for the addition (0.25% w/w) of neat paraffin.

Round aluminum trays were used to support the sample in the oven of the CL equipment. Isothermal chemiluminescence determinations were performed in air at 153°C in an oxyluminograph OL-94 instrument. Details of this equipment and of measurement procedure have been previously presented [5]. The meanings of kinetic parameters that are evaluated in this paper are presented in Fig. 1. This device allows determination of the dependence of photon counts on oxidation time.

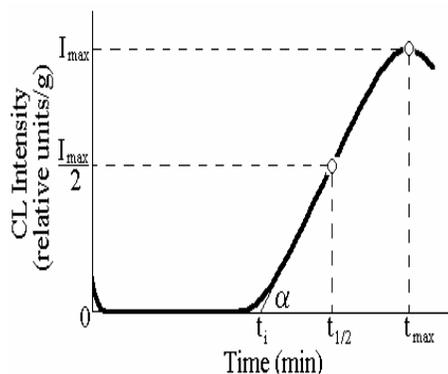


Fig. 1. The main kinetic parameters evaluated in this paper ($t_g a = v_{ox}^{max}$).

3. Results

The dependences of specific CL intensity on time for the studied extracts are presented in Fig. 2.

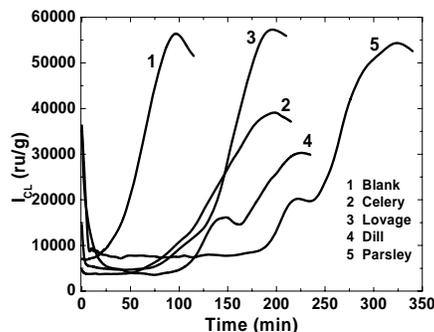


Fig. 2. Isothermal CL curves recorded at 153 °C in air for paraffin stabilized with studied extracts.

It can be noticed that the effect of dry extract from parsley on thermal stabilization of paraffin is more significant than the results for the addition of dry extracts from dill, lovage and celery.

Table 1 lists the main kinetic parameters calculated from CL measurements.

The mentioned extracts can be classified in three groups according to their stabilization efficiency. The first group consisting of parsley is characterized by the longest oxidation induction time and the lowest oxidation rate. The values of these parameters demonstrate their high capability to prevent oxidation. The second group of medium activity extracts includes dill and lovage. These extracts display moderate values of oxidation induction time and oxidation rate. The third group of extracts reveals very slight properties in the hindering of oxidation consist of celery.

Table 1. Kinetic parameters of thermal oxidation of paraffin in air at 153 °C. The paraffin was stabilized with the studied extracts.

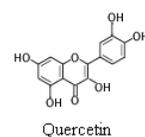
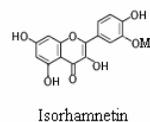
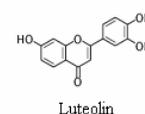
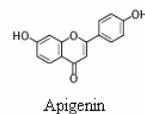
Extract	t_i (min)	$t_{1/2}$ (min)	V_{ox}^{max} (r.u/g min)	I_{max} (r.u/g)	t_{max} (min)
blank	5	33	982	56634	70
Petroselinum Crispum (parsley)	214	256	238	54554	320
Anethum Graveolens (dill)	120	164	343	30343	225
Levisticum Officinale (lovage)	115	148	923	53500	190
Apium Graveolens (celery)	56	96	803	65673	180

4. Discussion

Thermal stabilization of paraffin involves the efficient action of additives on the hindrance of the reaction between free hydrocarbon radicals and molecular oxygen. The appropriate protective activity is maintained on the induction time and on the propagation step when the concentration of oxygenated radicals becomes significant.

The antioxidant activity of flavonoids is related to their hydroxyl substitution of the aromatic A- and B- rings.

The chemical structures of the main flavonoids in plants of Apiaceae family are presented below [6]:



As is shown [7 – 9] the flavonoid content in these plants is given in Table 2.

As can be observed in Fig. 3 the total content of flavonoids in the studied plants it is in linear dependence to the length of the CL induction time.

Table 2. Flavonoids content in plants of Apiaceae family.

Plant denomination	Flavonoid content (mg/100g dry mass)							Reference
	Apigenin	Luteolin	Isorhamnetin	Kaempferol	Quercetin	Myricetin	Total	
Parsley (<i>Petroselinum Crispum</i>)	225.93	1.24	-	1.49	0.33	8.08	237.07	[7-9]
Dill (<i>Anethum Graveolens</i>)	-	-	43.5	13.33	55.15	0.70	112.68	[7, 9]
Lovage (<i>Levisticum Officinale</i>)	-	-	-	7.00	100.00	-	107.00	[7]
Celery (<i>Apium graveolens</i>)	2.41	-	-	-	0.18	-	2.59	[9]

The polyhydroxy substituted flavonoids present the highest antioxidant activity, while the most favorable structural characteristics appear to be the *o*-di-OH substitution on the B-ring [10]. Free radicals can abstract the two hydroxyl hydrogens of B-ring, producing the corresponding inactive quinones:

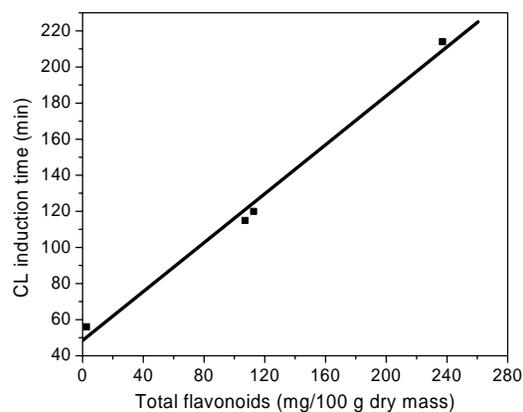
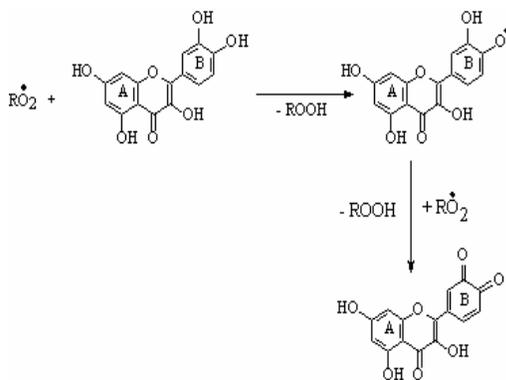


Fig. 3. Linear relation between CL induction time and total content of flavonoids in the studied plants of Apiaceae family.

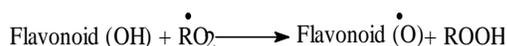
The positive relationship between increased hydroxylation and increased antioxidant activity of flavonols has also been reported in different oils [11].

The use of natural antioxidant packaging instead of other artificial ones like butylhydroxytoluene (BHT) and butylhydroxyanisole (BHA) improves the consumer health. For this reason, the trend is to use natural

antioxidants for food contact. The regulations and the directives of the EU tend to become stricter in respect of hazards due to the migration from packaging material to the packaged food. The studied extracts from plants in Apiaceae family have demonstrated good antioxidant properties. Later studies will be focused on the cooperative effects of the plant extracts and, with it, the behavior of the antioxidant packaging will be optimized from the chemical point of view.

5. Conclusions

The extract of *Petroselinum Crispum* (parsley) which contain highest amount of flavonoids (237 mg/100 g dry mass) exhibited the greatest antioxidant activity. The chemical composition showed a linear relationship between the total content of flavonoids and the antioxidant activity expressed as CL induction time. Based upon these observations and confirming evidence from the literature, we may conclude that flavonoids are oxidized by peroxy radicals, resulting in a more stable, less-reactive radical. Because of the high reactivity of the hydroxyl group of the flavonoids, radicals are made inactive, according to equation:



where $\overset{\bullet}{\text{R}}\text{O}_2$ is a peroxy radical and $\overset{\bullet}{\text{O}}$ is an oxygen free radical.

The determination of the antioxidant activity by chemiluminescence is advantageous because of its high sensitivity and rapidity. Nevertheless, the antioxidant activity measurements by chemiluminescence should be confirmed by other suitable methodologies.

References

- [1] W. Bors, M. Saran, *Free Radical Res. Comm.* **2**, 289 (1987).
- [2] C. A. Rice – Evans, N. Y. Miller, P. G. Bolwell, P. M. Branley, J. B. Pridham, *Free Radical Res. Comm.* **22**, 375 (1995).
- [3] S. V. Jovanovic, S. Steenken, M. Tomic, B. Marjanovic, M. G. Simic, *J. Am. Chem. Soc.* **116**, 4846 (1994).
- [4] L. Ramanathan, N. P. Das, *Int. J. Food Sci. Technol.* **28**, 279 (1993).
- [5] S. Jipa, T. Zaharescu, R. Setnescu, T. Setnescu, M. J. S. Brites, A. M. G. Silva, A. J. Marcelo – Curto, B. Gigante, *Polym. Int.* **48**, 414 (1999).
- [6] * * * USDA Database for the Flavonoid Content of Selected Foods, Maryland, USA, August 2006.
- [7] U. Justensen, P. Knuthsen, *Food Chem.* **73**, 245 (2001).
- [8] U. Justensen, P. Knuthsen, T. Leth, *J. Chromatogr. A.* **799**, 101 (1998).
- [9] A. Lugasi, J. Hovari, *Acta Alimentaria* **29**, 345 (2000).
- [10] D. Tsimogiannis, M. Samiotaki, G. Panyotou, V. Oreopoulos *Molecules* **12**, 593 (2007).
- [11] U. N. Wanasundara, F. Shahidi, *Food Chem* **50**, 393 (1991).

*Corresponding author: jipasilviu@yahoo.com