JOURNAL OF SCIENCE AND ARTS

VEGETAL EXTRACTS AS EFFICIENT PROTECTION IN OXIDATIVE DEGRADATION

SILVIU JIPA[1,2], TRAIAN ZAHARESCU[2], ELENA MANOLE[1], DAN ARTENIE MARIS[3]
MARIA MARIS[3], LAURA GORGHIU[1] AND CRINELA DUMITRESCU[1]
[1] "Valahia" University of Targoviste, Faculty of Sciences, Targoviste 130024
[2] INCDIE ICPE CA, 313 Splaiul Unirii, P. O. Box 149, Bucharest 030138
[3] "Ovidius" University of Constantza, Faculty of Dental Medicine, Constantza 900527

Abstract: *Several extracts from plants belonging to different families were obtained and their antioxidant activities in paraffin substrate were evaluated. The isothermal chemiluminescence at 153^{0}C was applied for the determination of the values for main kinetic parameters: oxidation induction time, maximum degradation time, demi-oxidation time, oxidation rate, maximum CL intensity. These characteristics allow establishing the contribution of extract components to the inhibition of oxidation in paraffin as a model compound for polymer materials.*

1. Introduction

The necessity of the improvement in polymer material durability is often solved by the addition of different compounds, which present antioxidant activity. There are several classes of synthetic stabilizers that delay degradation [1]. Fortunately, nature offers a large variety of structures that can be found in plants [2]. The extraction of these useful compounds belonging to various categories of polyphenols (flavonoids, polyphenolcarboxyl acids, anthocyanins, tannins, phenolamides) is a source for the protection against oxidative ageing [3]. Numerous studies were carried out on plants such as rosemary [4-6], sage [7-9], oregano [7, 10, 11], which resulted in a development of natural antioxidant formulations for food, medical wear, cosmetics, and other applications.

Polymer lifetime is controlled by both oxidation and mechanical degradation, mostly proceeding independently [12].The degree of material change is influenced by the intrinsic sensitivity of polymer to the individual stressors, by the intensity and duration of action, but also by the presence of stabilizer in the ageing matrix. For polyolefins, which cover the most part of polymer market, the mechanism of thermal degradation was reported by Bolland and Gee [13]. It is presented in the figure 1.

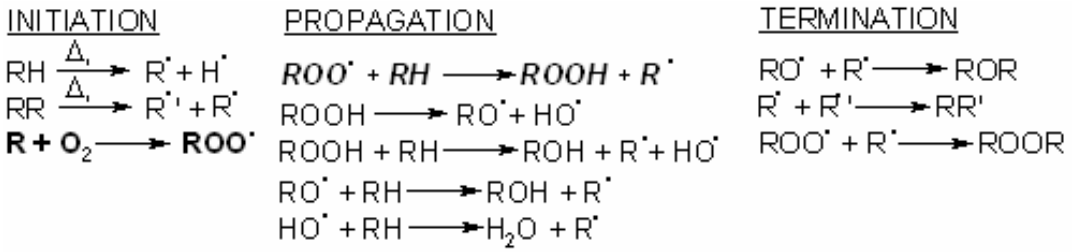

Figure 1. Degradation mechanism for polyolefins

The structures of polyphenols is proper configuration from which quinone products are formed after the conjugation of □ bonds of ring with C-O□ bond from originate phenolic group. Typical molecular configurations for flavonoids, which are main constituents of vegetal extracts are presented in figure 2.

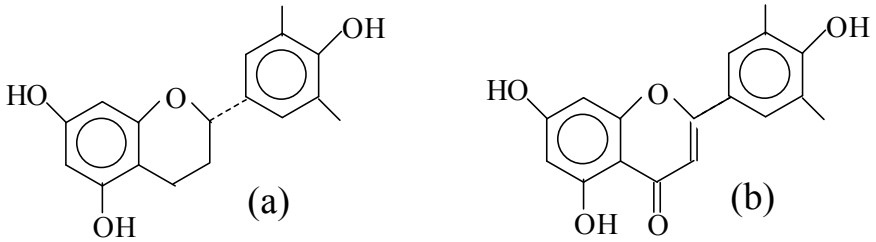

Figure 2. Typical structures for flavonoids. (a) catechine; (b) flavone

2. Experimental

10 g of dry vegetals were covered with 100 cm^3 of ethylic alcohol. The mixtures were let to stand for 5 days with intermittent shaking for homogenization. The final state of systems was subjected to filtration for the separation of alcoholic extract from vegetal matter. The liquid phase was placed into a vacuum dissicator for permanent removal of solvent till solid sample is obtained.
The addition of solid antioxidant into paraffin was performed by grinding it with appropriate amount of extract to attend the concentration of 0.25 %. An aliquate of 0.002 g was placed on round aluminum plate. The chemiluminescence measurements were performed with an equipment OL-94 unit built in our laboratory [14]. Isothermal determinations were carried out at 153^0C, either for control or for stabilized materials. The depencence of chemiluminescence intensity on the duration of thermal oxidation was obtained for each type of additived paraffin sample. The analysis of these curves allowed to evaluate kinetic parameters: oxidation induction time, oxidation rate, time of half oxidation level, maximum oxidation time and maximul CL intensity that characterize the progress of thermal oxidation in the standard polymeric material (paraffin).

3. Results and discussions

The oxidation process that takes place in paraffin follows the Bolland and Gee mechanism (figure 1). The attack of molecular oxygen, which exists or migrates from the reaction environment, reacts with free radicals appeared by the scission of some less tight bonds. The start of oxidation is depicted by the induction time of oxidation, when the amount of peroxyl radicals is not enough for a measurable oxidation rate.

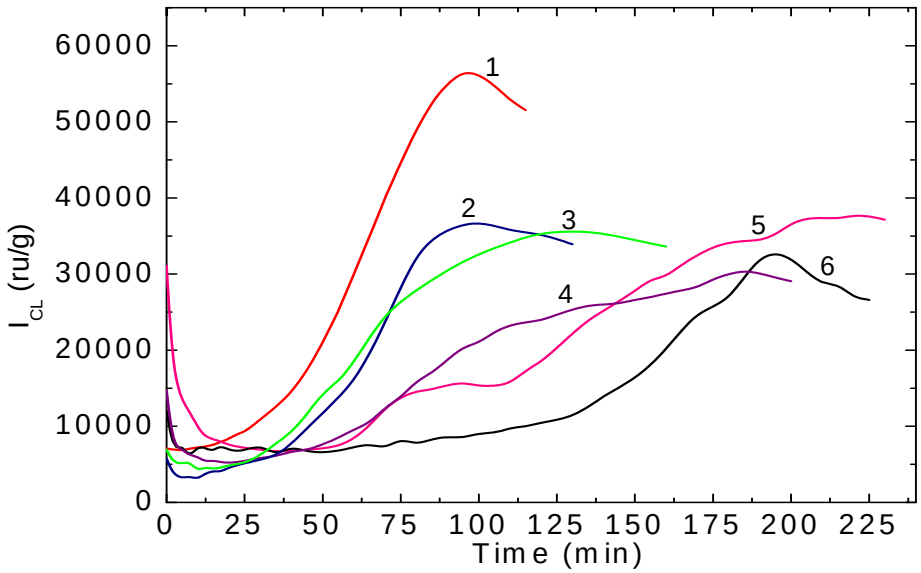

Figure 3. The chemiluminescence curves recorded for stabilized paraffin.
(1) free; (2) pimento; (3) caraway; (4) bay laurel; (5) thyme; (6) wild thyme.

This parameter (OIT) reveals the activity of stabilizer. The longer oxidation induction time characterizes the higher efficiency of additive. From table 1, the order of increasing the induction period places the obtained extracts in the following order:

caraway < pimento < bay laurel < thyme < wild thyme

The propagation of oxidation is sustained by the reaction of intermediates (figure 1), which advances due the involvement of hydroperoxides. The diminution of oxidation rate gets the possibility to reserve the stabilized products in direct relation with the propagation rate of oxidation. The sequence of studied extracts placed them on the other order base on the increasing of oxidation rates:

bay laurel < thyme ~ wild thyme < caraway < pimento

The differences noticed in the orders of efficiency suggests the availability of each antioxidant structure to provide other intermediates and their capacity towards the scavenging and blocking the reactive site on free radicals. The putative role of intermediates of presumed phenolic and quinoline structures is also brought up on whole duration of the thermal degradation of organic substrate. At the end of each thermal determination, the order of increasing maximum oxidation time:

pimento < caraway < bay laurel < wild thyme < thyme

Table 1. Kinetic parameters for thermal degradation of stabilized paraffin

Extract	Oxidation induction time, t_i (min)	Demi-period of oxidation, $t_{1/2}$ (min)	Oxidation rate, v_{ox}^{max} (u.r./g min)	Maximum CL intensity, I_{max} (u.r./g)	Maximum oxidation time, t_{max} (min)
Free	22	56	958	56634	95
Wild thyme (Thymus Serpillum)	100	150	380	31900	200
Thyme (Thymus Vulgaris)	67	122	369	37718	220
Bay laurel (Laurus Nobilis)	53	104	265	34000	175
Pimento (Pimento Officinalis)	42	63	787	37030	100
Caraway (Carum Carvi)	33	58	663	35644	132

It must be taken into consideration that the compositions of total phenolic fractions are different from one extract to the other, which influences the advance in the oxidation process (figure 3). Many studies are dedicated to the protective effects of vegetal antioxidants in relation with the total polyhenolic content [for example, 2, 3, 15-18]. This composition is very useful for the start of oxidation prevention, when new structures did not be formed. This kind of dosage must be applied during the whole period of stabilization in order to point out the structural modification occurred due to radical scavenging.

The general view on these data emphasizes the different behavior of plants belonging to different families. The extracts from Lamiaceae family, thyme and wild thyme, are the most efficient samples of investigated plant because their induction times are the longest periods and the the oxidation rates are sufficient low for low degradation effects.

The individual activity relative to the effects of largely used commercial antioxidant, TOPANOL OC, is also dependent on the content of flavonoids. Wild thyme has the highest relative activity (0.703); the other extracts exhibit various values between 0.405 and 0.099. It means that the Lamiaceae family is one of the most productive plants in relation with the efficient antioxidant components.

Several authors [19-22] identified different components in alcoholoc extracts of thyme and wild thyme:

- **Flavones:** xantomicrol, cirsimarin, cirsilineol, 5,4'-dihydroxy-7,4'-dimetoxy flavone, cuencvanin, timonin, apigenin-7-rutinosid, vicenin-2, luteolin-7-glucosid;
- **Flavonols:** quercetin;
- **Flavanones:** eriodictol, eriocitrin, hesperidin.

They present a remarcable antioxidant action in various conditions of chemical or biological environments. Some of representative molecular structures for studied extracts are displayed in figure 4.

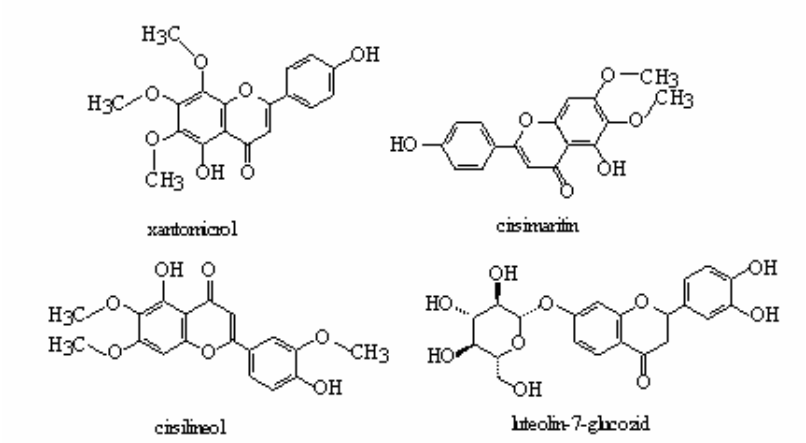

Figure 4. Some representative structures of antioxidants found in vegetal extracts

The active phenolic groups are placed on the left-side ring. They contribute to the screening of free radical activity in relation with the oxidative reactions. The influence of neighbour substituents would be decisive for the proton mobility and the antioxidant activity is in direct relation with the specific molecular structure. The facility in the descovering reactive positions for the trapping of free radicals will determine the level of oxidative protection. The conversion of initial phenolic structures into quinone configurations ensures an additional stabilization activity for these types of protection compounds.

4. Conclusion

The application of vegetal extracts for the thermal stabilization of polymers is based on the activity of polyphenolic components. They can retard oxidation by the reactions of phenolic hydroxyls and other active intermediates can be formed. The type of plant, the content of flavonoids and the proportion of components determine the antioxidant efficiency in polymer matrix. Antioxidant vegetal extracts present the great advantage of the lack of toxicity and the comparative activity for prevention of oxidative degradation. The beverage bottles or food packaging can be manufactured using these types of stabilizers because the global effects are favorable for human body and the additional contributions to the preservation of health may be beneficial.

5. Acknowledgment

This assay was performed in the frame of Partnership project 71-079, which belongs to the PNCDI II Program managed by NCPM.

References

[1] Herdan, M., Giurginca, M., and Meghea, A., *Antioxidants* (Roumanian edition), Technical printing House, Bucharest, 1982.
[2] Imark, C., Kneubühl, M., and Bodmer, S., *Innov. Food Sci. Emerging Technol.*, **1**, 239 (2001).
[3] Yu-Zhong Cai, Mei Sun, Jie Xing, Qiong Luo, and Corke, H., *Life Science*, **78**, 2872 (2006).
[4] Orhan, I., Aslan, S., Kartal, M., Bilge Şener, B., and Hüsnü Can Başer, K., *Food Chemistry*, **108**, 668 (2008).
[5] Pezo, D., Salafranca, J., and Nerín, C., *J. Chromatography A*, **1178**, 126 (2008).
[6] Bragagnolo, N., Danielsen, B., and Skibsted, L. H., *Innov. Food Sci. Emerging Technol.*, **8**, 24 (2007).
[7] Fasseas, M. K., Mountzouris, K. C., Tarantilis, P. A., Polissiou, M., and Zervas, G., *Food Chem.*, **106**, 1188 (2008).
[8] Durling, N. E., Catchpole, O. J., Grey, J. B., Webby, R. F., Mitchell, K. A., Foo, L. Y., and Perry N. B., *Food Chem.*, **101**, 1417 (2007).

[9] Vuković-Gačić, B., Nikčević, S., Berić-Bjedov, T., Knežević-Vukčević, J. and Simić, D., *Food Chem. Toxicol.*, **44**, 1730 (2006).
[10] D'Oca, M. C., Bartolotta, A., Cammilleri, M. C., Brai, M., Marrale, M., Triolo, A., and Parlato, A., *Food Control*, **18**, 996 (2007).
[11] Su, L., Yin, J. –J., Charles, D., Zhou, K., Moore, J., and Yu, L., *Food Chem*., **100**, 990 (2007).
[12] White, J. R., and Rapoport, N. Y., *Trends Polym. Sci*., **2**, 197 (1994).
[13] Bolland, J. L., and Gee, G., *Proc. Royal Soc. (London)*, **186**, 230 (1946).
[14] Gorghiu, L. M, Mihalcea, I., Jipa, S., Setnescu, R., Zaharescu, T., and Setnescu, T., *Rev Chim (Bucharest)* **53**, 587 (2002).
[15] Netzel, M., Netzel, G., Tian, Q. G., Schwarz, S., Konczak, I., *Innov. Food Sci. Emerging Technol.*, **8**, 339 (2007).
[16] Amić, D., Amić, D., D., Bešlo, D., and Trinajstić, N., *Croat. Chim. ActaI,* **76**, 55 (2003).
[17] Ayaz, F. A., Hayirlioglu-Ayaz, S., Alpay-Karaoglu, S., Greúz, J., Valentová, K., Ulrichová, J., and Strnad, M., *Food Chem*., **107**, 19 (2008).
[18] Santos-Gomez P. C., Seabra, R. M., Andrade, P. B., and Fernandes-Ferreira, M., *Plant Sci*., **24**, 851 (2004).
[19] Crăciunescu, O., Buzgariu, W., Buiculescu, R., Coroiu, V., and Moldovan, L., *Romanian Biol.Sci*., **III**, 20 (2005).
[20] Arora, R., Chawla, R., Sagar, R., Prasad, J., Singh, S., Kumar, R., Sharma, A., Singh, S., and Sharma, R.K., *Molec.Clee.Biochem*., **273**, 209 (2005).
[21] Choi, D. W., Leininger-Muller, B., King, Y. C., Leroy, P., Siest, G., Wellman, M., *Free Radical Res*., **36**, 893 (2002).
[22] http://www.sanatateata.com/plante/chimion.htm