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NATURAL EXTRACTS AS POTENTIAL SOURCE OF ANTIOXIDANTS TO STABILIZE POLYOLEFINS

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INTRODUCTION

Polymers and especially polyolefins need the addition of antioxidants in their formulations to provide protection during processing or fabrication to finished product [1]. Usually, hindered phenols are added to polyolefins to manage the oxidation reaction for long-term protection while organophosphites are added as short-term antioxidants. If the polyolefins are used in packaging food, these compounds or their degradation products could migrate from plastics into foodstuffs during processing or storage. Therefore, in the last years, instead of the synthetic antioxidants usuallly employed, natural ones are being investigated to reduce the problems associated with the contamination of the food.

OBJECTIVE

The aim of this work is to study the potential of several natural matrixes as sources of antioxidants to use as plastic additives.

The matrixes studied were: green tea, black tea, *Lippia citriodora* and *Hyericum androsaemum*. The phenolic profiles were studied by High Performance Liquid Chromatography (HPLC) using ultraviolet (UV) diode array and Fluorescence (FL) detectors.

COMPARISON OF ANTIOXIDANT ACTIVITY OF PLANTS' EXTRACTS

Sample preparation

3.0 g of each powdered sample were boiled for fifteen minutes in 300 mL of water and then filtered over a Büchner funnel. The resulting extract was lyophilized. A yield of 0.9-1.1 g was obtained.

DPPH• scavenging activity

The antiradical activity of the extracts was determined spectrophotometrically by monitoring the disappearance of DPPH• at 515 nm, according to a previously described procedure [2]. The plate was incubated for 30 min at room temperature. Three experiments were performed in triplicate.

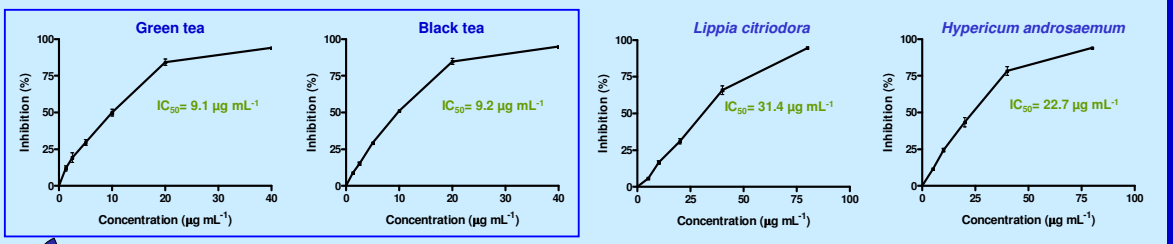

Figure 1. Effect of the extract on DPPH reduction. Values show mean ±SE from three experiments performed in triplicate (aqueous extract).

Samples of tea showed higher antioxidant activity than the other considered extracts

ANALYSIS OF THE EXTRACTS BY HPLC

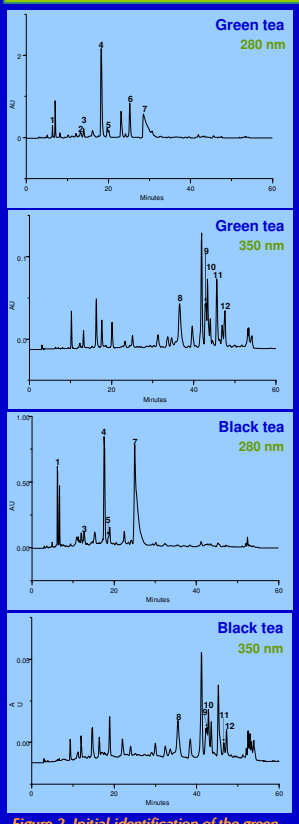

Figure 2. Initial identification of the green and black tea extracts by HPLC-UV.

Table I. Identified compounds in tea extracts by HPLC-UV

Peak	Compound	Wavelength
1	Gallic acid	280 nm
2	Catechin*	
3	Epigallocatechin	
4	Epigallocatechingallate	
5	Epicatechin	
6	Epicatechingallate	
7	Caffein	
8	Myricetin glucoside	350 nm
9	Quercetin glucoside	
10	Quercetin rutinoside	
11	Kaempferol glucoside	
12	Kaempferol rutinoside	

* Peak is not pure

A qualitative analysis of the phenolic profile of the tea extracts, that showed the highest antioxidant activity, was performed by HPLC with a UV diode array detector. Reverse phase chromatography was employed. The system solvent used was a gradient of water/formic acid (19:1) and methanol [3].

The identified compounds are shown in figure 2 and table 1: as it was expected, the most abundant compounds seem to be the flavanols.

Phenolic profile of the extracts of *Lippia citriodora* and *Hyericum androsaemum* were previously reported [4, 5] with high content in flavonols.

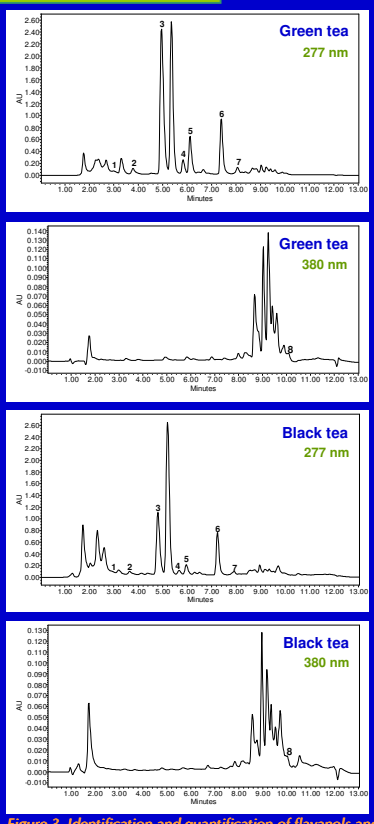

Figure 3. Identification and quantification of flavanols and quercetin in the green and black tea extracts by HPLC-UV-FL.

Table 2. Concentration of flavanols and quercetin in natural extracts determined by HPLC-UV-FL

Peak		[ ] / mg compound g-1 sample							
		Green tea		Black tea		*Hyericum*		*Lippia*	
		PDA	FL	PDA	FL	PDA	FL	PDA	FL
1	(-)-Epigallocatechin	*	29,2	*NQ*	4,95	*ND*	*ND*	*ND*	*ND*
2	(+)-Catechin	3,47	2,89	0,93	0,67	0,95	0,58	*ND*	*ND*
3	(-)-Epigallocatechingallate	72,0	*ND*	13,3	*ND*	*ND*	*ND*	*ND*	*ND*
4	(-)-Epicatechin	5,5	5,23	0,75	0,96	0,49	0,46	*ND*	*ND*
5	(-)Gallocatechingallate	10,5	*ND*	*NQ*	*ND*	*ND*	*ND*	*ND*	*ND*
6	(-)-Epicatechingallate	13,1	10,3	4,84	4,59	*ND*	*ND*	*ND*	*ND*
7	(-)-Catechingallate	*NQ*	*ND*	*NQ*	*ND*	*ND*	*ND*	*ND*	*ND*
	Total flavanols	105	47,6	19,8	11,2	1,45	1,04	*ND*	*ND*
8	**Quercetin**	0,043	*ND*	*NQ*	*ND*	0,71	*ND*	*ND*	*ND*

•Peak not pure;
ND: not detectable; NQ: not quantificable

According to Vinson et al. [6] flavanols have higher antioxidant activiy than flavonols, and quercetin is the flavonol that shows to be a better antioxidant. Therefore, the second part of the chromatographic study was focused on the determination of flavanols and quercetin in the considered extracts using a HPLC method with two detectors, UV diode array and fluorescence (FL), to avoid the interferences and improve the detection limits of the method (figure 3). Reverse phase chromatography with methanol:water as mobile phase was used [7].

Concentration of the flavanols and quercetin decreased in the order green tea, black tea, *Lippia citriodora* and *Hypericum androsaemum* (table 2). So, green tea extract showed the highest content in flavanols and the highest antioxidant capacity.

CONCLUSIONS

I. Extracts of green and black tea showed higher antioxidant capacity than other considered plants: *Lippia citriodora* and *Hypericum androsaemum*.

II. An analytical method using HPLC-UV-FL was used to quantify flavanols and quercetin in the considered extracts, compounds that theoretically show the highest antioxidant capacity. Their content decreased in the same order than their antioxidant activity.

III. A extract of green tea was added as antioxidant to a polypropylene film: the stability of the material was comparable to the one stabilised with synthetic antioxidants, showing the interest of this matrix as a potential source of natural antioxidants for plastics.

USE OF GREEN TEA EXTRACT AS ADDTIVE OF POLYPROPYLENE

Use of green tea extract was tested as an additive to protect polypropylene (PP) against the oxidation. 5 films made of polypropylene were extruded and re-extruded until 4 times and their Melt Flow Index (MFI) was measured to check their stability.

The film additived with green tea extract was compared with films additived with the natural antioxidants catechin or epicatechin, with the mixture of synthetic antioxidants Irganox 1076 and Irgafos 168 and with a film not stabilized (table 3).

After 4 extrusions pass, catechin have shown the best performance to stabilize PP. The green tea extract showed a good behavior, even better than the mixture Irganox 1076 and Irgafos 168.

Table 3. Additives concentration in the PP film

Additive	Concentration (%)
Not stabilized	----
Green tea extract	0.05
(+)-Catechin	0.05
(-)-Epicatechin	0.05
Irganox 1076	0.1
Irgafos 168	0.1

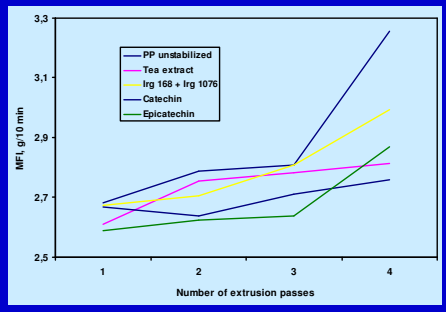

Figure 4. Stability of PP with different antioxidants or green tea extract [8].

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