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Antioxidant activity of biphenolic compounds anchored on mesoporous alumina

Vanina A. Guntero [1,2], Cristián A. Ferretti [1,*], Carla Ormachea [1], Pedro M.E. Mancini [1] and María N. Kneeteman [1]

[1] IQAL (UNL-CONICET), Laboratorio Fester – QUÍMICA ORGANICA (FIQ), Universidad Nacional del Litoral, Santa Fe, Argentina
[2] Universidad Tecnológica Nacional (UTN) – Facultad Regional San Francisco, Grupo Productos Naturales, San Francisco, Argentina
* cferretti@fiq.unl.edu.ar; Tel.: +54-342-457-1164

Abstract: Phenolic antioxidants are used in the industry to delay the oxidation of fats being the most used butyl hydroxy anisole (BHA) and butyl hydroxy toluene (BHT). However, the consumer concern respect their safety has motived to study natural alternatives. In this sense, the aim of this work was to evaluate the behavior of 3,3'- dimethoxy-5,5'-di-2-propenyl-1,1'-biphenyl-2,2'-diol and 6,6'- dihidroxi-5,5'-dimethoxy-(1,1'-biphenyl)-3,3'-dicarbaldehyde free and supported on mesoporous alumina. Biphenolic compounds were synthetized by radical coupling and then anchored on alumina by microwave assisted process. The antioxidant activity of these compounds was investigated by phosphomolybdenum method. The results showed that biphenolic compounds anchored on mesoporous alumina have a marked antioxidant activity better than free antioxidants. Biphenolic compounds supported on alumina display antioxidant properties and hence have the potential for use as a food preservative, beverage, cosmetics and pharmaceutical industries.

Keywords: antioxidant activity, phosphomolybdenum method, biphenolic compounds.

1. Introduction

Additives are substances which are added on foods with a technological objective or to provide a functional property. In this sense, antioxidants are added to foods for minimize rancidity, retard the formation of toxic oxidation products, maintain nutritional quality, and increase shelf life[1].

It is known that methoxyphenols are antioxidant. They owe their activity to the ability to trap the chain-carrying peroxy radicals (ROO·) by donation of the phenolic hydrogen atom reaction (Eq. (1)), which is a very much faster reaction than the attack of the peroxy radicals on the organic substrate (RH)[2].

$$\begin{aligned} ROO^{\bullet} + ArOH &\longrightarrow ROOH + ArO^{\bullet} \\ ROO^{\bullet} + RH &\longrightarrow ROOH + R^{\bullet} \\ 2\,ROO^{\bullet} &\longrightarrow \text{non radical products} \end{aligned} \quad (1)$$

Phenolic compounds could react with free radicals such as ROO·,RO·,OH· and O_2^{-} much faster than the phospholipid that is always present at much higher quantities in living cells than the antioxidant[2]. Nowadays the industry uses synthetic antioxidants. However, natural products are increasingly demand for consumers. In this sense, the aim of this work was to evaluate the behavior

of two biphenyl compounds, 3,3'- dimethoxy-5,5'-di-2-propenyl-1,1'-biphenyl-2,2'-diol (BiEG) and 6,6'- dihidroxi-5,5′-dimethoxy-(1,1'-biphenyl)-3,3'-dicarbaldehyde (BiVA) free and supported on mesoporous alumina (MA).

Mesoporous alumina was choose because it has suitable structure, large specific surface area and high pore volume enable high loading of active species [3]. Its stability leads to better dispersion, biocompatibility and subsequent functionalization [4].

2. Materials and Methods

2.1. Synthesis of biphenolic compounds

The synthesis of biphenolic compounds was realized by radical coupling following [5][6]. Mesoporous alumina was synthesized in accordance with the published procedure [7] using Pluronic P123 as template. In a typical experiment, the triblock copolymer Pluronic P123 (3 g) and aluminum trichloride (0,4 g) were dissolved in 60 mL of ethanol under stirring at 40°C. Then, aluminum isopropoxide (6 g) was added to the solution. The solution was maintained at 40 °C for 2 h, and the surfactant was removed by calcination, which was carried out by increasing the temperature to 400 °C for 4 h. The supporting of phenolic compounds on mesoporous alumina were performed by a microwave assisted oven procedure [8].

2.2. Characterization of biphenolic compounds

Biphenolic compounds (BiEG and BiVA) were checked by melting points and spectroscopic studies (IR, 1H-NMR, 13C-NMR). The equipment used to determinate FTIR was a Shimadzu FTIR Prestige-21 spectrophotometer and magnetic resonance nuclear were made on a Bruker DPX-300.

2.3. Determination of antioxidant activity

The assay was carried out by phosphomolibdene method which is based on the reduction of Mo(VI) to Mo(V) by the sample and the formation of a green complex. Decrease of absorbance is directly proportional of antioxidant activity of sample [9]. Briefly, the method consisted of prepare solutions of biphenolic compounds in ethanol. Then mix 1 mL of sample solution, 9 mL of reactive solution and incubate at 95 °C for 120 min. The absorbance was measure at 695 nm against a blank on a Perkin Elmer Lambda 20 spectrophotometer. Results obtained were compared with BHT. Antioxidant activity was expressed as inhibition (I) calculated by the equation where As is initial absorbance, As120 is the absorbance of the sample at 120 min, Ac is initial absorbance of control and Ac120 is the absorbance of control at 120 min (Eq. (2)).

$$I\ (\%) = \frac{1-(A_S-A_{S120})}{(A_C-A_{C120})} \quad (2)$$

2.4. Characterization of materials

Materials free and with biphenolic compounds anchored were characterized by nitrogen adsorption/desorption isotherms. The measurements were performed with a NOVA-1000 Quantachrome at liquid nitrogen temperature (77 K). The specific surface areas of the samples were calculated using the Brunauer Emmett Teller (BET) method in the relative pressure range of 0.05 0.35. The pore size distribution (PSD) curves were derived from the adsorption branches of the isotherms using the Barrett Joyner Halenda (BJH) method. The pore volumes were obtained from the adsorption branches of the isotherms at a partial pressure of 0.99. Small angle X-ray scattering patterns (SAXS) were realized with a XEUSS 1.0, with Cu K radiation of wavelength 1.54178 Å.

2. Results and Discussion

Results obtained by FTIR, melting points and NMR confirmed the structures and purity of the compounds.

N_2 adsorption/desorption isotherms of materials are shown in the Table 1. BiVA and BiEG anchored on mesoporous alumina caused the reduction on BET surface, on pore volume and on the average pore diameter, which is attributed to the biphenolic compounds found inside the pores of the alumina, reducing the adsorption of nitrogen and consequent the textural parameters of alumina free.

Table 1. Textural parameters of materials.

Sample	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (Å)
MA	266	0,90	136
BiVA-MA	180	0,10	22
BiEG-MA	157	0,54	158

The small angle patterns indicate the presence of channel type wormlike. For the sample with BiEG and BiVA, the presence of these compounds on MA rises to a decrease in the diffracted intensity (Figure 1).

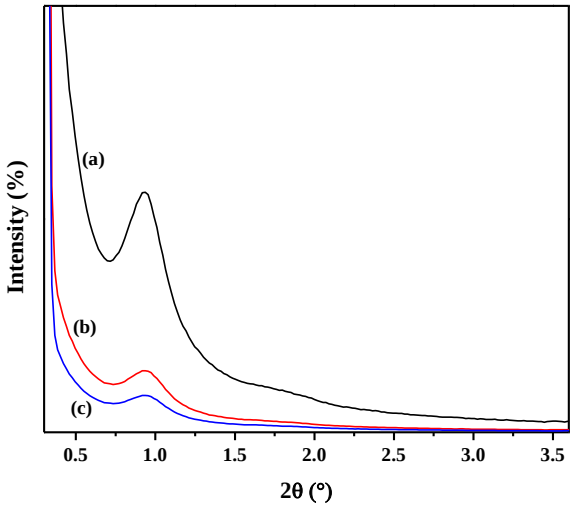

Figure 1. Small angle X-ray scattering patterns of a) AL, b) BiVA-AL, c) BiEG-AL.

To evaluate the antioxidant activity of synthetized materials the phosphomolybdenym method was used. Alumina did no showed antioxidant activity. BiVA and BiEG presented antioxidant properties. Biphenolic compounds anchored on mesoporous alumina presented higher antioxidant activity than those free compounds.

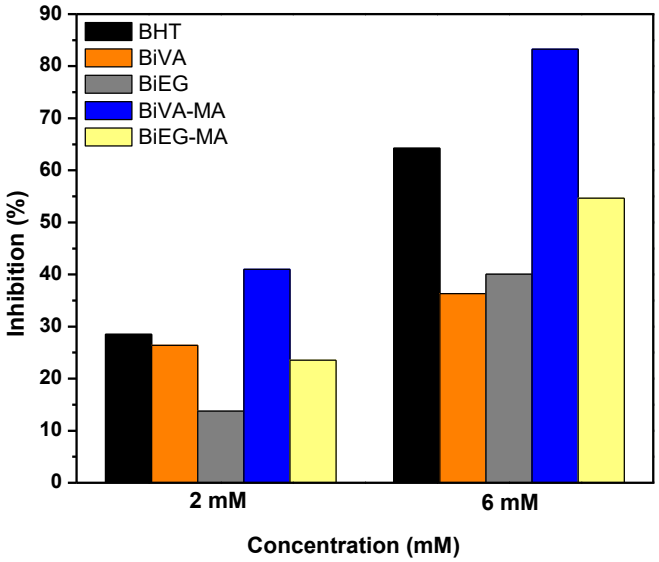

Figure 2. Antioxidant activity of biphenolic compounds free and anchored on mesoporous alumina.

3. Conclusions

In summary, biphenolic compounds were synthesized and then anchored on mesoporous alumina through a microwave assisted process. The physicochemical characterization of these materials confirmed the successful anchored of the compounds into the mesoporous alumina. These systems show higher antioxidant properties when they are anchored on mesoporous alumina opening like this new opportunity of application in packaging.

Acknowledgments

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Conflicts of Interest: The authors declare no conflict of interest.

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