



# Impact of natural sources-derived antioxidants on the oxidative stability and rheological properties of castor oil based-lubricating greases

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## ABSTRACT

It is well known that spontaneous oxidation is one of the main drawbacks for the industrial use of eco-friendly vegetable oil-based lubricants. Herein a quick and easy synthesis of different molecules belonging to stilbene family is reported, which together with a number of representative natural sources-derived products with antioxidant (AO) capacity have been tested as additives for improving the oxidative stability of a selected bio-lubricating grease formulation. Thus, different gel-like dispersions based on N-acylated chitosan in castor oil also including these additives have been prepared. Gel-like dispersions were characterized through thermogravimetric analysis (TGA), oxidation onset temperature (OOT) and small-amplitude oscillatory shear (SAOS) rheological measurements. These preliminary results demonstrate that, in general, these antioxidants delay N-acylated chitosan-based gel-like dispersions oxidation. However, the AO activity is more relevant in the case of propyl gallate and ascorbic acid palmitate and not so important in the family of stilbene derivatives. On the other hand, the addition of any antioxidant does not qualitatively affect the rheological response but unexpectedly may significantly modify the values of the SAOS functions. Remarkably, the delay of oxidation reactions occurs by exclusively employing natural resources-derived components, being these formulations environmentally acceptable as a whole and potentially employed in specific industrial applications.

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## 1. Introduction

In previous studies, acylated chitosan gel-like dispersions in castor oil were introduced as promising eco-friendly alternatives to traditional lubricating greases, where the thickening properties were imparted by this modified biopolymer, instead of the well-known metallic soaps whereas the castor oil was used as biodegradable base oil (Sánchez et al., 2014, 2015). One of the main drawbacks of vegetable oils to act as efficient and effective lubricants is the poor oxidative stability. Despite that additives are usually included in small proportions, the development of green multifunctional additives for lubricant formulations has also gained

special attention in order to improve specific properties of vegetable oil-derived base oils (Karmakar and Ghosh, 2013, 2015; Li et al., 2014; Singh et al., 2014; Delgado et al., 2014), the thermo-oxidative stability among them.

In the field of natural products, an antioxidant (AO) may be defined as any compound capable of preventing or retarding the oxidation of a biological substrate or molecule initiated by any reactive compound, either free radicals or other species that are capable of initiating or inducing the oxidation of any substrate (Galano, 2009; Nagaraju and Belur, 2009). From a wide point of view, molecules able to reduce oxidation phenomena can act through different mechanisms and may be roughly classified as primary antioxidants, or chain-breaking radical scavengers; secondary antioxidants, also named oxygen scavengers and peroxide decomposers; and those which act through a combination of the functionalities of both of them. In this work, any substance able to

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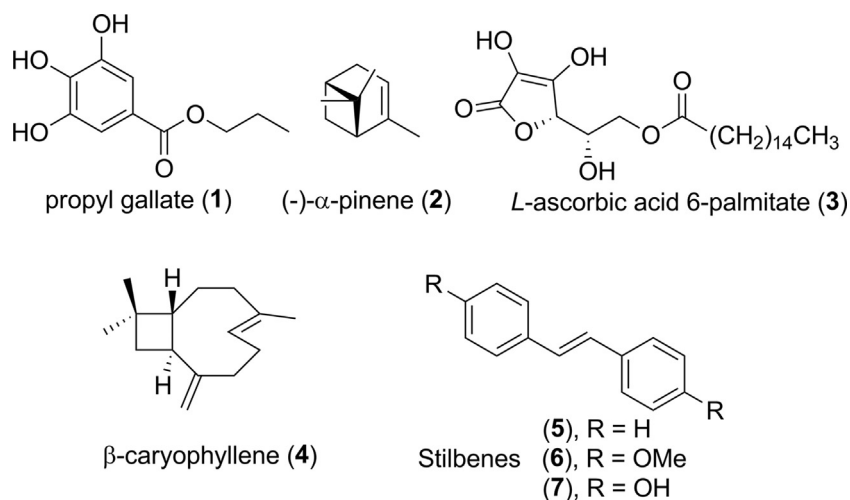


Fig. 1. Antioxidant (AO) compounds selected for the study.

prevent or damp oxidation independently of the action mechanism is considered a potential AO.

The use of AOs as additive in catalytic proportions can help to prevent the oxidative processes that lubricants are usually subjected. Numerous attempts have been made to improve oxidative stability of vegetable oils for industrial purposes by using synthetic antioxidant additives, i.e., butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), *tert*-butylhydroquinone (TBHQ) or 4,4'-methylene bis(2,6-di-*tert*-butylphenol) (MBP) (Ruger et al., 2008; Dunn, 2005; Fox and Stachowiak, 2007; Merrill et al., 2008; André et al., 2010; Quinchia et al., 2011). To meet the criteria of green chemistry an ideal option is selecting AO compounds belonging to the family of natural products. Many naturally occurring compounds are well known to be used in the manufacture of biodegradable lubricant formulations. For instance,  $\alpha$ -tocopherol, propyl gallate and ascorbyl palmitate were previously tested as AOs in several vegetable oils and compared to more traditional synthetic antioxidants like MBP, resulting comparable AO activity in some cases (Quinchia et al., 2011). Dunn (2005) also pointed out similar effectiveness of propyl gallate and BHA as antioxidants in biodiesel formulations obtained from soybean oil, with BHA showing advantage at higher loadings. On the other hand, Ruger et al. (2008) found higher effectiveness of TBHQ in soybean oil than BHT and ascorbyl palmitate at different temperatures. In general, it can be deduced that propyl gallate is a well-tested natural compound with effectiveness comparable to the conventional synthetic antioxidants. Besides this, it can be expected that different natural products possessing different AO activity including a number of derivatives of stilbene family (Schultz et al., 1990) could be used as potential AO agents that retard oxidation phenomena in lubricating greases (Valgimigli and Pratt, 2012).

Mechanistically, the ability to act as AO depends on both the possibility of release of H atoms, and on the ability to trap  $R^{\bullet}$  in the whole molecule skeleton (Iuga et al., 2012). Therefore, it is evident that there is a strong relationship between the chemical structure of a molecule and its potential to act as AO. Among natural sources-derived AO molecules, compounds such as propyl gallate (1), (-)- $\alpha$ -pinene (2), L-ascorbic acid 6-palmitate (3),  $\beta$ -caryophyllene (4) together with three low functionalized components of the family of stilbenes (5–7) have been selected in this work (see Fig. 1). Some of them hold neighboring –OH or other functional groups, whereas the stilbene skeleton corresponds to one of the most prominent families responsible of a wide variety of biological and pharmacological activities (Tan et al., 2007; Schmitt et al., 2010; Csiszar, 2011). Altogether form a representative selection of several

molecules with different chemical structures, which come from different species in the world of plants, and have different well-known antioxidant capacity referred to pure products. The antioxidant activity of natural products could be globally related to either the presence of hydroxyl (–OH) groups in the structure (1, 3, and 7, in Fig. 1), which can scavenge free radicals produced in vivo, or to the presence of “active” positions (allylic, benzylic, unsaturations, etc.; 2, 4, and 5, in Fig. 1) that can rapidly interact with oxidative radicals, thus preventing the oxidation processes (Amorati et al., 2013). The most common structural modification observed in aromatic –OH groups of naturally occurred active compounds is their methylation (6, in Fig. 1), which may result in a partial loss of most representative bioactivities. This happens not so strictly in the field of antioxidant activity, which may even be increased by means of this modification (Stivala et al., 2001; Krivogorsky et al., 2011).

Therefore, the main objective of this work was to test the AO activity of the above referred natural sources-derived compounds in a selected novel bio-based lubricating grease formulation based on castor oil as base oil and acylated chitosan as thickener agent. Apart from their AO performance some unexpected influences of these compounds on the thermal degradation and rheological response of the final formulation were analyzed.

## 2. Materials and methods

As an overall experimental description, commercial AO samples together with others chemically modified from the stilbene family were added to gel-like dispersions based on castor oil and acylated chitosan. First, non-commercial AO samples were chemically synthesized and original chitosan modified by acylation. Afterwards, gel-like dispersions of the acylated chitosan in castor oil, also containing small amounts of the AO samples analyzed, were prepared and characterized by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and rheological measurements.

### 2.1. Materials and instrumentation

Castor oil from Guinama (Spain) and chitosan from Qingdao Yunzhou Biochemistry Co. Ltd. (China) were used to prepare the gel-like dispersions studied. The average molecular weight and degree of deacetylation of the chitosan were  $2.29 \times 10^5$  g/mol and 86.3%, respectively. Decanoyl chloride, supplied by Sigma-Aldrich, was used to chemically modify chitosan. Propyl gallate (1, Fig. 1), (-)- $\alpha$ -pinene (2, Fig. 1), L-ascorbic acid 6-palmitate (3, Fig. 1),  $\beta$ -

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