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Antioxidant potency of gallic acid, methyl gallate and their combinations in sunflower oil triacylglycerols at high temperature

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ABSTRACT

Lipid peroxidation and polar compounds formation in sunflower oil triacylglycerols at 120 °C were investigated in the presence of gallic acid (GA), methyl gallate (MG), MG/GA combinations (75:25, 50:50, and 25:75), and *tert*-butylhydroquinone (TBHQ). Hydroperoxide-based kinetic parameters (IP, induction period, min; k_i, rate constant during IP, meq/kg min) of control sample (38.0; 2.0346) were considerably improved by TBHQ (201.1; 0.0267), followed by GA (163.8; 0.0837), MG (151.2; 0.0983), and the combinations (~184.4; ~0.0861) with an average synergy of 18.6%. Regarding the polar compounds inhibition, the best antioxidant performance (the ratio of IP to oxidized triacylglycerol monomers at IP, min/%; time reaching 10% of triacylglycerol dimers and polymers, min) in general belonged to MG/GA 75:25 (42.4; 263.0), GA (43.2; 249.9), MG (38.0; 237.5), and TBHQ (17.7; 214.4), respectively. The kinetic parameters based on the formation of polar compounds than hydroperoxides provided more reliable results to evaluate antioxidant potency at high temperature.

1. Introduction

Gallic acid (3,4,5-trihydroxybenzoic acid, GA) and its methyl ester derivative, methyl gallate (MG), are among the prevalent phenolic compounds in plant kingdom (Chanwitheesuk, Teerawutgulrag, Kilburn, & Rakariyatham, 2007; Rahman, Jeon, & Kim, 2016). They are well known for a wide range of valuable biological effects such as antioxidant, anti-inflammatory, anti-apoptotic, anti-microbial, anti-tumor, and anti-platelet activities, protection against DNA damage and lung injury due to oxidative stress, and attenuation of diabetic oxidative stress (Rahman et al., 2016; Rajan & Muraleedharan, 2017).

A limited number of studies conducted in recent years have shown GA and MG to considerably prevent lipid oxidation under normal storage conditions (Asnaashari, Farhoosh, & Sharif, 2014; Farhoosh, Johnny, Asnaashari, Molaahmadibahraseman, & Sharif, 2016; Roidoung, Dolan, & Siddig, 2016). Additionally, a previous hydroperoxide-based evaluation of GA and MG indicated their impressive ability to improve a number of thermal kinetic parameters of lipid oxidation (Farhoosh, Sharif, Asnaashari, Johnny, & Molaahmadibahraseman, 2016). Thermal treatments, which are frequently used to process food materials, can drastically affect the antioxidant efficiencies. Therefore, antioxidants of high potency under such a harsh condition have always been of special interest. *tert*-Butylhydroquinone [2-(1,1-dimethylethyl)-1,4-benzenediol, TBHQ] is known to be one of the most powerful synthetic antioxidants employed widely in food industry and also considered to have really good resistance to thermal decomposition and/or volatilization (Ying et al., 2010). Nevertheless, due to possible toxic and carcinogenic effects of synthetic antioxidants, TBHQ is not allowed for food application in many countries (Pinho, Ferreira, Oliveira, & Ferreira, 2000).

Lipid hydroperoxides, or primary oxidation products, are unstable intermediates that easily decompose into a variety of secondary oxidation products. The latter will not significantly be produced unless the concentration of hydroperoxides (meq/kg, called as peroxide value, PV) reaches a critical point, PV_{IP} (Fig. 1A), at the end of the initiation phase of lipid peroxidation (Marquez-Ruiz, Martin-Polvillo, & Dobarganes, 2003). The time distance to this point is called induction period, IP, which is the time before rapid deterioration in the propagation phase of lipid peroxidation onwards. During IP, hydroperoxides slowly increase with a rate constant k_i (Fig. 1A) (Shim & Lee, 2011).

At high temperatures, a more complex group of oxidation products of mainly higher polarity is produced. The analysis of polar compounds is one of the most reliable methods of lipid oxidation monitoring under thermally harsh conditions. Polar compounds are two sets of alteration components formed through thermoxidative reactions and hydrolytic cleavage of triacylglycerols. The first set is comprised of oxidized

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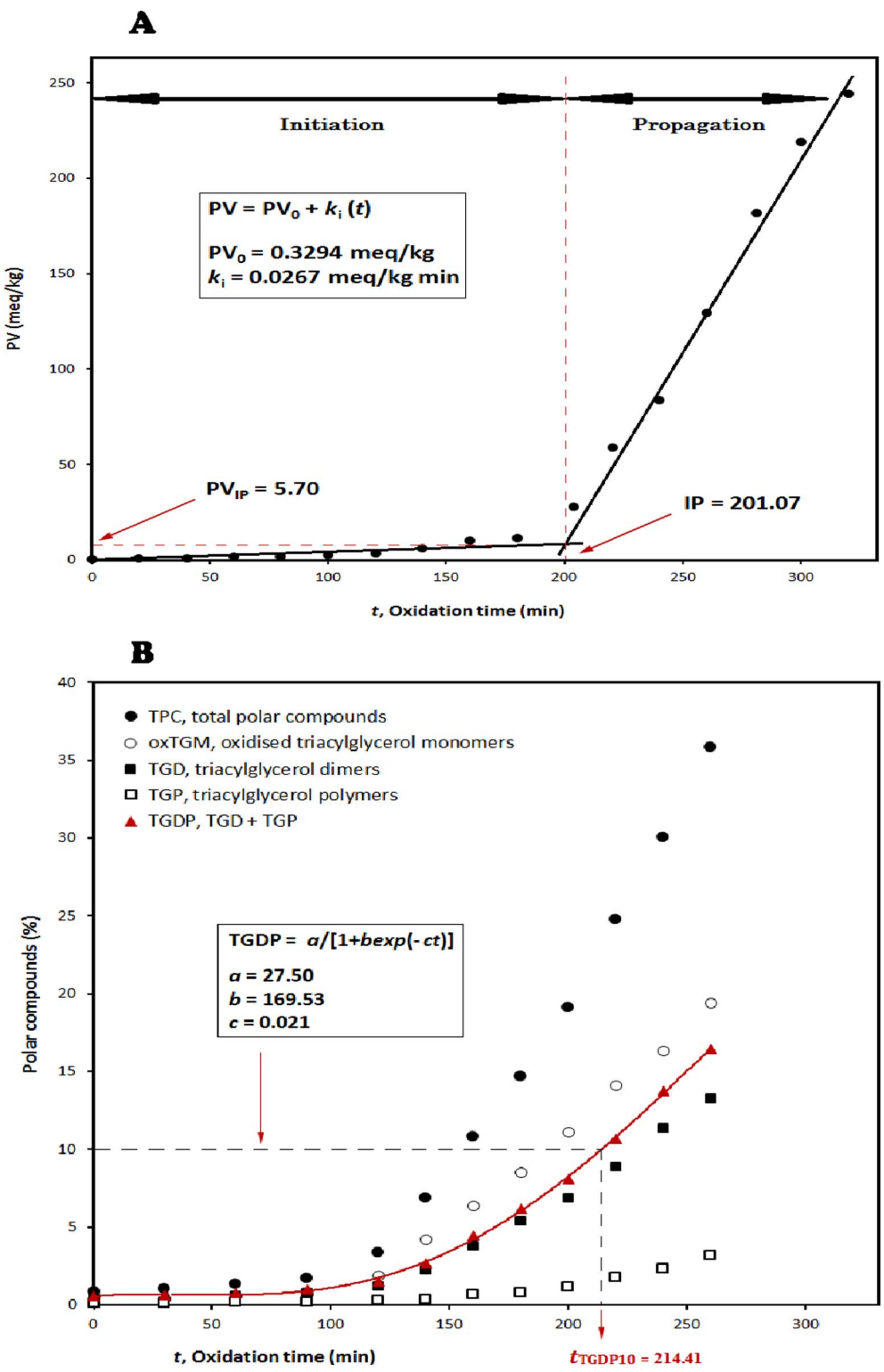

Fig. 1. Kinetic curves of accumulation of hydroperoxides (A) and polar compounds (B) during the oxidation of the purified sunflower oil containing 0.6 μM of *tert*-butylhydroquinone, TBHQ, at 120 °C. PV_0, PV, and PV_{IP}: the concentrations of hydroperoxides at the beginning, after time *t*, and at the induction period, IP, respectively; k_i: the rate constant of hydroperoxide formation during IP; t_{TGDP10}: the time required to reach a TGDP content of 10%.

triacylglycerol monomers (oxTGM), triacylglycerol dimers (TGD), and triacylglycerol polymers (TGP), and the second one consists of diacylglycerols (DG) and free fatty acids (FFA) (Houhoula, Oreopoulou, & Tzia, 2003) (Fig. 1B). The oxTGM, in turn, encompass a wide range of oxidation products with one or more oxygenated functional groups, such as peroxide group in lipid hydroperoxides, or epoxy, keto, or hydroxyl groups in many of secondary oxidation products. Hence, oxTGM measurement can be used to determine total oxidation, which provides concomitant useful information on initial and advanced stages of lipid oxidation. Dimeric, TGD, and polymeric, TGP, components, which are very complex and structurally not fully identified, are characteristic of advanced oxidation. Polymerisation compounds have been shown to increase as the amount of oxTGM reduces during the course of oxidation. In other words, more reactive molecules of oxTGM are polymerised at high temperatures through oxygenated linkages (Ruiz-Mendez, Marquez-Ruiz, & Dobarganes, 1997). A TGDP (TGD + TGP) content of 10% is a criterion that has received much attention nowadays (Farhoosh & Tavassoli-Kafrani, 2011) because feeding trials