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Comparison of the effect of sinapic and ferulic acids derivatives (4-vinylsyringol vs. 4-vinylguaiacol) as antioxidants of rapeseed, flaxseed, and extra virgin olive oils

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ABSTRACT

The aim of the work is to compare the antioxidant activity of 4-vinylguaiacol (4-VQ) and 4-vinylsyringol (4-VS) added to stabilize three (flaxseed, olive and rapeseed) commercial oils. The phenolics were added at concentration of 20, 40 and 80 mg per 100 g of oil. The oils were oxidized in a Rancimat test at 110 °C. The linear dependences between the concentrations of each of these compounds and the induction period (IP) were found. Generally, 4-VQ was more effective, since the determined IP increase after its addition was from 5 to 25-fold higher than for the same addition of 4-VS. The highest increase was noted for flaxseed oil, for which 80 mg 4-VQ addition per 100 g of oil resulted in 50% IP increase. The highest absolute values of IP were reached by extra virgin olive oil, naturally abundant in phenolic compounds and with the lowest fatty acids oxidation index.

1. Introduction

Plant oils recommended for the human diet should supply a proper composition of unsaturated fatty acids and various pro-healthy compounds. There is a growing market of oils extracted from unconventional sources or produced by more conservative methods, such as cold-pressing. In relation to plant source, they are characterized by specific color, flavor, fatty acids composition and composition of lipid-soluble minor compounds such as sterols, tocols, carotenoids, squalene, polyphenols, chlorophylls, free fatty acids and metal ions. The composition of these oils affects their nutritional attractiveness and determines their oxidative stability during storage (Choe & Min, 2006; Prescha, Grajzer, Dedyk, & Grajeta, 2014).

Many recent studies have shown that the oxidative stability of plant oils is highly related to their abundance in phenolic compounds. Farhoosh and Hoseini-Yazadi (2013) showed that oxidative stability of olive oil was primarily related to phenolic compounds and/or tocopherol content. Gruzdiene and Anelauskaite (2011) found a strong correlation ($r = 0.94$) between induction time and total phenolics in rapeseed oils. A similar phenomenon was noted by Roszkowska, Tańska, Czaplicki, and Konopka (2015) for 21 market rapeseed oils, for which tocopherols and carotenoids (known as typical hydrophobic antioxidants) had no significant effect. Furthermore, Dąbrowski, Konopka, Czaplicki, and Tańska (2017) showed that chia oil obtained by extraction with acetone, with the highest amount of phenolics, was characterized by higher oxidative stability than cold-pressed, hot-pressed and hexane extracted, and oils extracted by super fluid extraction (SFE-extracted oils).

However, the content of phenolic compounds in oil is highly differentiated by method of its production. For rapeseed oil, the available data varied in this regard from only traces (Roszkowska et al., 2015) up to above 8000 mg/kg (Gruzdiene & Anelauskaite, 2011). Generally, the lowest amounts were found for cold-pressed oils, which contain up to 25 mg/kg of these compounds (Roszkowska et al., 2015; Siger, Nogala-Kalucka, & Lampart-Szczapa, 2008). Farhoosh, Einafshar, and Sharayei (2009) for various hexane-extracted rapeseed oils determined the total content of phenolics ranging from ca. 24 to 127 mg/kg. Market rapeseed oils contained from zero up to 323 mg/kg of these compounds (Roszkowska et al., 2015). The use of more polar solvents, such as acetone and hot-pressing or microwave treatment before pressing or extraction, increases the concentration of phenolic compounds in oil (Niu, Jiang, Wan, Yang, & Hu, 2013; Zheng, Yang, Zhou, Liu, & Huang, 2014). The main phenolic compounds in rapeseed oil are sinapic acid and its derivatives (Niu et al., 2013). Kraljić et al. (2015) found that in crude rapeseed oil, 4-vinylsyringol (canolol) is the dominant compound, accounting for 85% of total phenolics. This compound is preferentially accumulated in rapeseed oils obtained after thermal, pressure or microbial seed pre-treatment (Galano, Francisco-Márquez, & Alvarez-Idaboy, 2011). For example, microwave treatment of seeds can increase the canolol yield from 50 to 800 mg/kg of pressed rapeseed oil (Zheng et al., 2014). In contrast, refining can decrease the total content of phenolic

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compounds by 90% (Kraljić et al., 2015). In deodistillate of rapeseed oil, 4-vinylsyringol dimer prevails, followed by sinapic acid and 4-vinylsyringol (Harbaum-Piayda et al., 2010).

Similar variation in phenolic compounds was noted, for example, for flaxseed and olive oils. The cold-pressed flaxseed oils contain from ca. 4 to 22 mg/kg of phenolic compounds (Siger et al., 2008; Tańska, Roszkowska, Skrajda, & Dąbrowski, 2016) to as high as 768 to 3073 mg/kg (Choo, Birch, & Dufour, 2007). According to various authors, the major phenolics of this oil are: *p*-hydroxybenzoic, vanillic and ferulic acids (Siger et al., 2008); vanillic acid (Tuberoso, Kowalczyk, Sarritzu, & Cabras, 2007) and vanillin (derivative of ferulic acid) (Hasiewicz-Derkacz et al., 2015). The minor phenolic components in this oil are non-hydrolysable proanthocyanidins and hydrolysable tannins, *p*-coumaric acid, caffeic acid, coniferyl- and syringaldehyde and small amounts of flavonoids (Hasiewicz-Derkacz et al., 2015). Olive oils contain up to 495 mg of phenolic compounds per kg in relation to plant source, agriculture treatment and technology of oil extraction (Najafi, Barzegar, & Sahari, 2015). Among them, approx. 50 various phenolic compounds were identified such as flavonoids, phenolic alcohols and acids, secoiridoids, lignans and their metabolites (Cerretani, Toschi, & Bendini, 2009).

Canolol, as the product of sinapic acid decarboxylation, may be found in oils from seeds of the *Brassicaceae* family (Nićiforović & Abramovič, 2014). More ubiquitous in the plant kingdom is ferulic acid, which exists in all lignocellulose components of plant cells (Konopka, Tańska, Faron, & Czaplicki, 2014), and its thermal or enzymatic/microbial decarboxylation leads to formation of 4-vinylguaiacol (Coghe, Benoot, Delvaux, Vanderhaegen, & Delvaux, 2004). These abilities have, for example, *Lactobacillus brevis* strains (Curiel, Rodríguez, Landete, de las Rivas, & Muñoz, 2010), *L. farciminis* (Hadiza, Shahid, Kim, & Maznah, 2012) and *Bacillus coagulans* BK07 (Karmakar et al., 2000). Accumulation of 4-vinylguaiacol is inherent to the beer production process (Coghe et al., 2004). This compound is also formed during thermal (roasting at 180 °C) degradation of curcumin (besides of vanillin and ferulic acid) (Esatbeyoglu, Ulbrich, Rehberg, Rohn, & Rimbacha, 2015).

In recent years, there has been a growing interest in natural phenolic derivatives with high antioxidant properties. The presence of methoxy- and hydroxyl groups in the structure of polyphenols improves their antioxidant ability (Karamać, Kosińska, & Pegg, 2005; Terpinc et al., 2011). 4-vinylsyringol contains additional metoxy group in position 2 (Fig. 1). Although both of these compounds are assayed as effective antioxidants in the emulsion system (Terpinc et al., 2011) we did not found a comparison of their activity in oil matrices.

The main aim of the present work is to compare the antioxidant activity of 4-vinylguaiacol and 4-vinylsyringol against three various oils (flaxseed, olive and rapeseed) in in a Rancimat test conducted at 110 °C. Although, this test was criticized as being unreliable to oil oxidation mechanism at typical storage conditions (Frankel, 1993), nowadays is popular and frequently used because of its simplicity, also for kinetic studies (Gharby et al., 2016; Symoniuk, Ratusz, & Krygier, 2017).

2. Materials and methods

2.1. Oil samples and phenolic acid derivatives

The experimental materials included four samples of commercial oils (three bottles of each type) from the local market in Poland: two types of rapeseed oils (refined and cold-pressed, produced in Poland), cold-pressed flaxseed oil (produced in Poland) and extra virgin olive oil (produced in Italy). According to the manufacturer, the oils were of a suitable shelf life. The oils were analyzed after opening the packaging and kept between analyses in a freezer (at −20 °C).

The phenolic acid derivatives used in the study were commercially available as analytical standards with a declared purity > 95%. The 4-vinylguaiacol (2-methoxy-4-vinylphenol) purchased from Sigma-Aldrich (Poznań, Poland) and the 4-vinylsyringol (4-ethenyl-2,6-dimethoxyphenol) purchased from EnamineStore (Riga, Latvia). The HPLC chromatograms presented in Fig. 1 confirm the high purity of these compounds.

2.2. Oxidation test

Before the oxidation test, the phenolic acids derivatives were dissolved in acetone (HPLC grade purity, purchased from Sigma-Aldrich) and added to each oil sample (200 g) to obtain a final concentration of 20, 40 and 80 mg of 4-vinylguaiacol or 4-vinylsyringol per 100 g of oil.

An accelerated oxidation test was evaluated on a Rancimat apparatus 743 (Metrohm, Herisau, Switzerland). The oil sample (2.5 g) was weighed in a reaction vessel and was capped and placed in a thermostatic electric heating block at 110 °C. An air flow rate of 20 L/h was given. Determination of the induction period (IP) was based on the conductometric detection of volatile oxidation products. The time that elapsed until these oxidation products appeared was saved as the induction period.

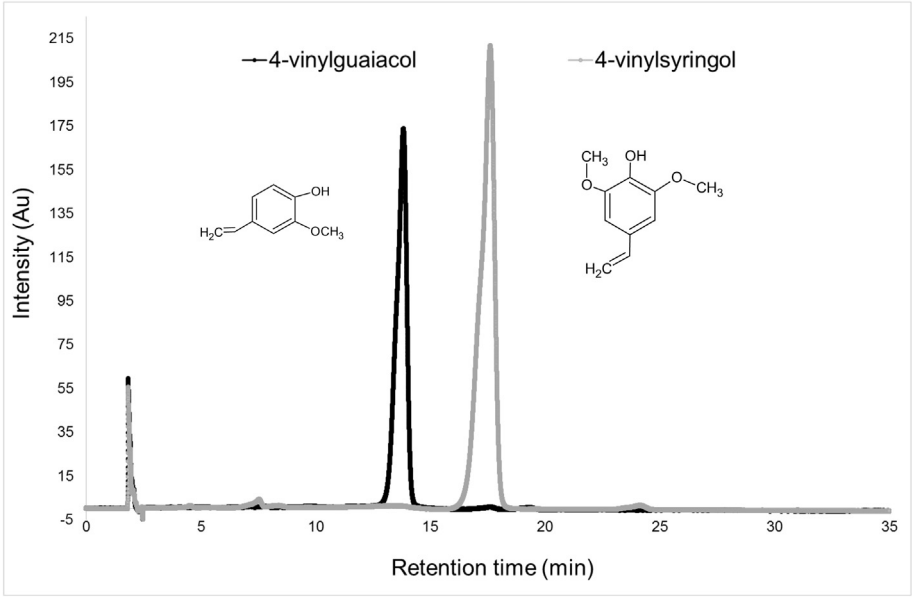

Fig. 1. Chromatograms of used standards of phenolic acid derivatives (4-vinylsyringol and 4-vinylguaiacol), and their structural formulas.