EFFECT OF CANOLOL (4-VINYLSYRINGOL) ON THE OXIDATION OF EDIBLE OILS

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Abstract
Rapeseed contains high amounts of phenolic compounds, mainly derivatives of sinapic acid, but only a small part can be found in virgin rapeseed oil, since the polar compounds remain in the press cake. A temperature treatment of the raw material results in the degradation of sinapic acid to 2,6-dimethoxy-4-vinylphenol (vinylsyringol or canolol), which is described in literature as a very strong antioxidive component. This compound shows good oil solubility and passes over into the oil during pressing. In the present work canolol was measured together with the tocopherols by HPLC and detected by fluorescence detector. During the heat-treatment the content of tocopherols was not affected while the content of canolol continuously increased with simultaneous decrease of sinapic acid. Higher amounts of canolol in rapeseed oil strongly improved the oxidative stability of the oil in the Rancimat test at 120°C. Canolol showed a significant antioxidant effect in the ß-carotene-linoleic acid assay.

Key words: Canolol, rapeseed oil, oxidation stability, roasting

Introduction

Rapeseed oil is one of the most important vegetable oils in the world and behind palm oil and soybean oil on the third position of the world production. Additionally to different bioactive compounds such as tocopherols and phytosterols, the seeds contain comparatively high amounts of phenolic compounds (Naczk et al., 1998), with sinapic acid (3,5-dimethoxy-4-hydroxycinnamic acid) as main component in free or esterified form as sinapine, the choline-ester of sinapic acid. Artz et al. (1986) and Matthäus (1998) showed that phenolic compounds are mainly located in the cotyledons and they found only traces in the seat coats.
Recently another derivative of sinapic acid came into the focus of interest because of its highly potent antioxidative activity and the antimutagenic and anticarcinogenic properties (Kuwahara et al., 2004; Vuorela et al., 2003; Cao, et al, 2008). 2,6-dimethoxy-4-vinylphenol (vinylsyringol) or canolol was firstly identified in two independent studies from Koski et al. (2003) and Wakamatsu et al. (2005) in crude rapeseed oil. Kuwahara et al. (2004) described the antiradical and antimutagenic potency of this compound as higher than for α-tocopherol, ß-carotene, vitamin C and different flavonoids like rutin or quercetin. The compound is formed by decarboxylation of sinapic acid during heating of rapeseeds resulting in high amounts of canolol in cold-pressed rapeseed oil from roasted seeds or in crude rapeseed oil from big oil processing facilities resulting from the conditioning process to improve oil yield (Vuorela, et al., 2003; Koski et al., 2003; Wakamatsu et al., 2005).

Determination of canolol

Different methods for the determination of canolol are available (Vuorela et al., 2003; Spielmeyer et al., 2009) which base on the extraction of the phenolic compounds by methanol/water and determination by HPLC with UV-detection. Since canolol shows a good solubility in nonpolar solvents like petroleum ether or n-hexane it is possible to determine the compound in rapeseed oil together with the tocopherols accordingly to the method of Balz et al. (1992). A solution of about 10 mg oil in 1 mL of a solution of 4.85 µg/mL 2,2,5,7,8-pentamethyl-6-chromanol as internal standard in n-heptane was directly used for the HPLC. The HPLC analysis was conducted using a Merck-Hitachi low pressure gradient system, fitted with a L-6000 pump, a Merck-Hitachi F-1000 Fluorescence Spectrophotometer (detector wavelengths for excitation 295 nm, for emission 330 nm) and a Chromgate integration system (Knauer, Berlin, Germany). 20 µL of the samples were injected by a Merck 655-A40 Autosampler onto a Diol phase HPLC column 25 cm x 4.6 mm ID (Merck, Darmstadt, Germany) used with a flow rate of 1.3 mL/min. The mobile phase used was n-heptane/tert. butyl methyl ether (99+1, v/v). The quantification of canolol took place in regard to the internal standard and the results were expressed as mg canolol per 100 gram rapeseed or rapeseed oil. Figure 1 shows a typical HPLC chromatogram of virgin rapeseed oil from unroasted seeds.

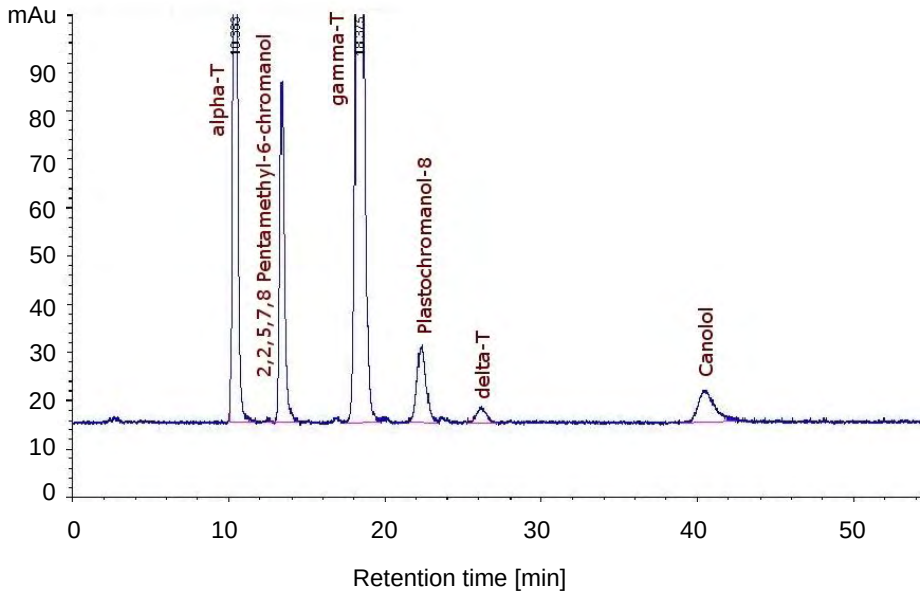

Figure 1: HPLC chromatogram of a virgin rapeseed oil from unroasted seeds

Formation of canolol during heating of rapeseed

Figure 2 shows the effect of heating on the formation of canolol in rapeseed as a function of the time at 180 °C and the simultaneous degradation of sinapic acid. After about 10 minutes the content of canolol in the seeds increased linear with the duration of heat-treatment. The temperature used for roasting seems to have no effect on content and composition of tocopherols in the resulting rapeseed oil (Wakamatsu et al., 2005; Spielmeyer et al., 2009). Possibly canolol acts as antioxidant to protect the tocopherols from degradation during the heating process.

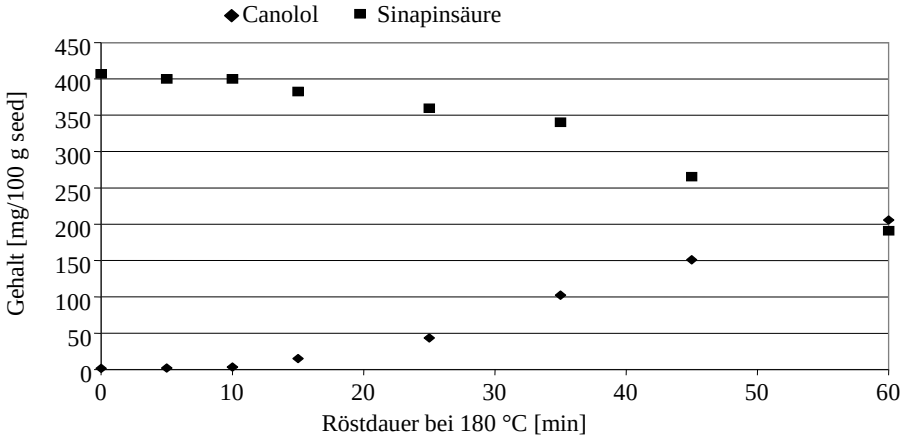

Figure 2 Influence of heat-treatment during roasting on the degradation of sinapic acid and formation of canolol

Antioxidative activity of canolol

In literature canolol is described as an effective antioxidant (Kuwahara et al., 2004; Koski et al.; 2003; Wakamatsu, et al., 2005; Vuorela et al., 2005). In the present work pure canolol was obtained by purification of a canolol containing oily extract from roasted rapeseed by gel permeation chromatography. Figure 3 shows that canolol is suitable to reduce the degradation of carotene in the ß-carotene-linoleic acid assay significantly. The antioxidant activity is comparable to the sinapic acid, but not as good as for BHT or trolox used for comparison.

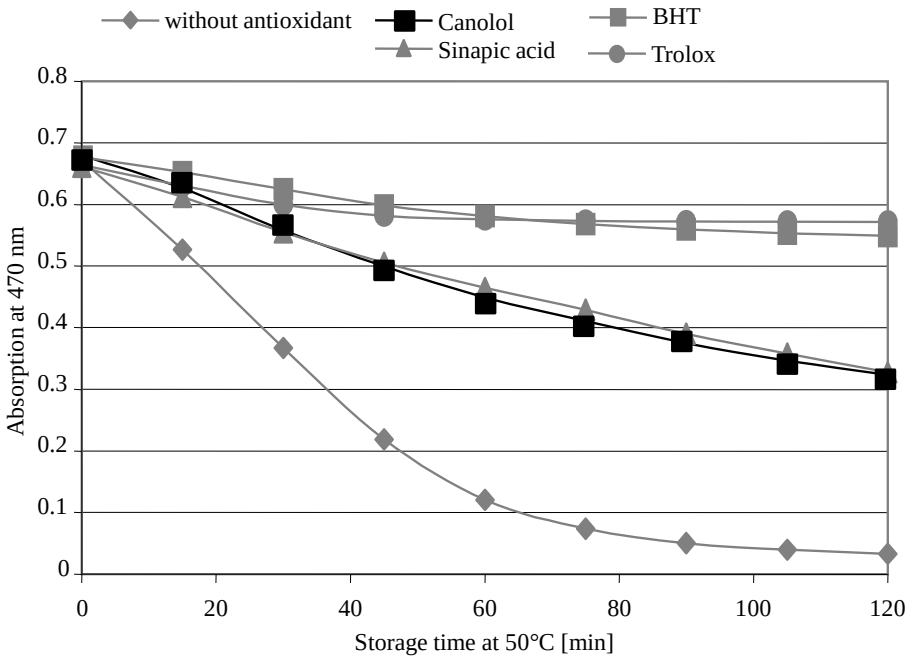

Figure 3: Purified canolol from oil of roasted rapeseeds: ß-carotene-linoleic acid assay

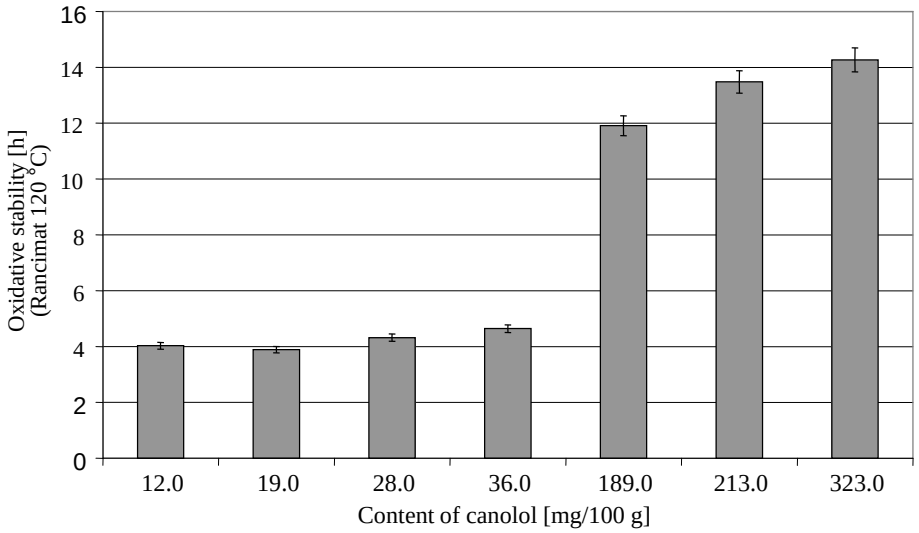

Figure 4: Influence of the content of canolol on the oxidative stability of rapeseed oil in the Rancimat test (120 °C)

Figure 4 presents that the oxidative stability of rapeseed oil increases with increasing amounts of canolol. While canolol contents between 12.0 and 36.0 mg/100 g oil only resulted in a slight increase of the oxidative stability, amounts of about 200 mg/100 g oil and higher improved the oxidative stability of the oil remarkable.

Conclusions

The finding of canolol by Koski et al. (2003) and Wakamatsu et al. (2005) in rapeseed oil from heat-treated raw material could be an interesting way to improve oil quality in view of health aspects but also with regard to oxidative stability. The formation of canolol in rapeseed results in a higher oxidative stability of the resulting oil in the Rancimat test and pure canolol has a significant antioxidative activity. Temperatures between 160 and 180°C in the raw material are necessary during the heat-treatment to form remarkable amounts of canolol, whereas content and composition of the tocopherols are not affected by the treatment. The results show that roasting of rapeseeds before production of cold-pressed rapeseed oil could result in an added-value product with a higher nutritional value and a higher oxidative stability during storage.

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