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DETERMINATION OF COUMARIN IN CINNAMON AND CINNAMON-CONTAINING PRODUCTS

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INTRODUCTION

Cinnamon, as a spice and as an additive to various food groups such as breakfast cereals, teas and bakery products is an important part of the human diet. Cinnamon, among many other bioactive components, contains an important active compound coumarin. Coumarins are a class of compounds that contain a 1,2-benzopyrone skeleton. Numerous studies have shown that coumarin has a beneficial health effect on the body in optimal concentration, but its increased long-term consumption can lead to adverse health effects. In this study, the amount of coumarin in ten different food products found on the Croatian market, including ground spices and teas, was analyzed. Also, different extraction parameters were analyzed in order to find the best method of extraction of coumarin from ground cinnamon and cinnamon containing products.

MATERIAL

Ten samples were obtained from Croatian retail market in 2019. Samples include ground cinnamon, cinnamon teas and cinnamon juice.

Table 1. List of marks, products, producers and types of packaging

Mark	Product	Packaging	Producer
C1	Ground cinnamon	Glass	Kotanyi
C2	Ground cinnamon	Glass	Vegeta
C3	Ground cinnamon	Paper bag	AGZ
C4	Ground cinnamon	Glass	Revita
C5	Ground cinnamon	Paper bag	Kotanyi
C6	Ground cinnamon	Paper bag	Nadalina
C7	Cinnamon orange clove tea	Paper bag	Podravka
C8	Cinnamon apple tea	Paper bag	Podravka
C9	Cinnamon apple tea	Paper bag	Franck
C10	Cinnamon apple juice	Plastic bottle	Maraska

EXTRACTION OF COUMARIN

Two types of extraction techniques were used to determine the optimal extraction conditions: ultrasound-assisted extraction (UAE) and extraction by heating and stirring using two solvents, methanol and ethanol at 30 and 50 °C for 30 and 50 min. The weight of all samples was 500 mg and the volume of solvent used was 1 mL. Each extraction was performed in two samples. After determining the optimal conditions, the other samples were extracted with methanol, namely 500 mg of sample in 1 ml of solvent for 10 min at 30 and 50 °C. After extraction, the samples were centrifuged for 5 min at 5000 rpm, then decanted whereby the supernatants were collected in glass flasks and stored at 4 °C until the HPLC analysis.

CONCLUSION

The most effective method of extraction of coumarin from ground cinnamon was with methanol as a solvent at a temperature of 30 °C (50°C for teas) for 10 min using stirring on a magnetic stirrer. The content of coumarin in ground cinnamon corresponds to the content of coumarin in Ceylon cinnamon. Compared to ground cinnamon, teas have a lower coumarin content due to the lower content of cinnamon in teas, although the content of coumarin in teas is significantly higher compared to the research which indicates the use of a larger amount of cinnamon or the use of cassia cinnamon. Coumarin was not found in the apple cinnamon juice Amarena (C10) or is below the detection level, which indicates a low content of cinnamon in the juice.

HPLC DETERMINATION OF COUMARIN

The sample extracts were filtered through 0.2 µm PTFE filter. The analysis was performed on an Agilent 1260 Infinity II. The HPLC system used for the analysis consisted of a quaternary pump (G7111A), a column chamber (G7116A), an autosampler (G7157A), a photo-diode array (DAD) detector (G7115A) and a fraction collector (G1364E). Chromatographic separation was performed on a Cosmosil 5C18-MS-II (Nacalai Tesque) column (250 x 4.6 mm) filled with 5 µm particles. Separation was achieved by gradient elution at a flow rate of 1mL/min, and a 1% solution of acetic acid in water and methanol was used as the mobile phase. A standard coumarin (Sigma Aldrich, USA), purity ≥ 99%, was used to construct the calibration curve. The retention time of the coumarin standard was 18.085 min. Separation was performed in a column heated to 25 °C, and coumarin detection was performed at a wavelength of 300 nm, with spectrum recording in the wavelength range from 190 nm to 400 nm. 20 µL of sample was injected into the device. Sample analyzes were performed in duplicate, and two injections were performed from each prepared solution. The results of the content of coumarin in the analyzed samples are expressed in mg/kg. Linearity of the calibration curve was confirmed by R^2 = 0. 9966.

RESULTS

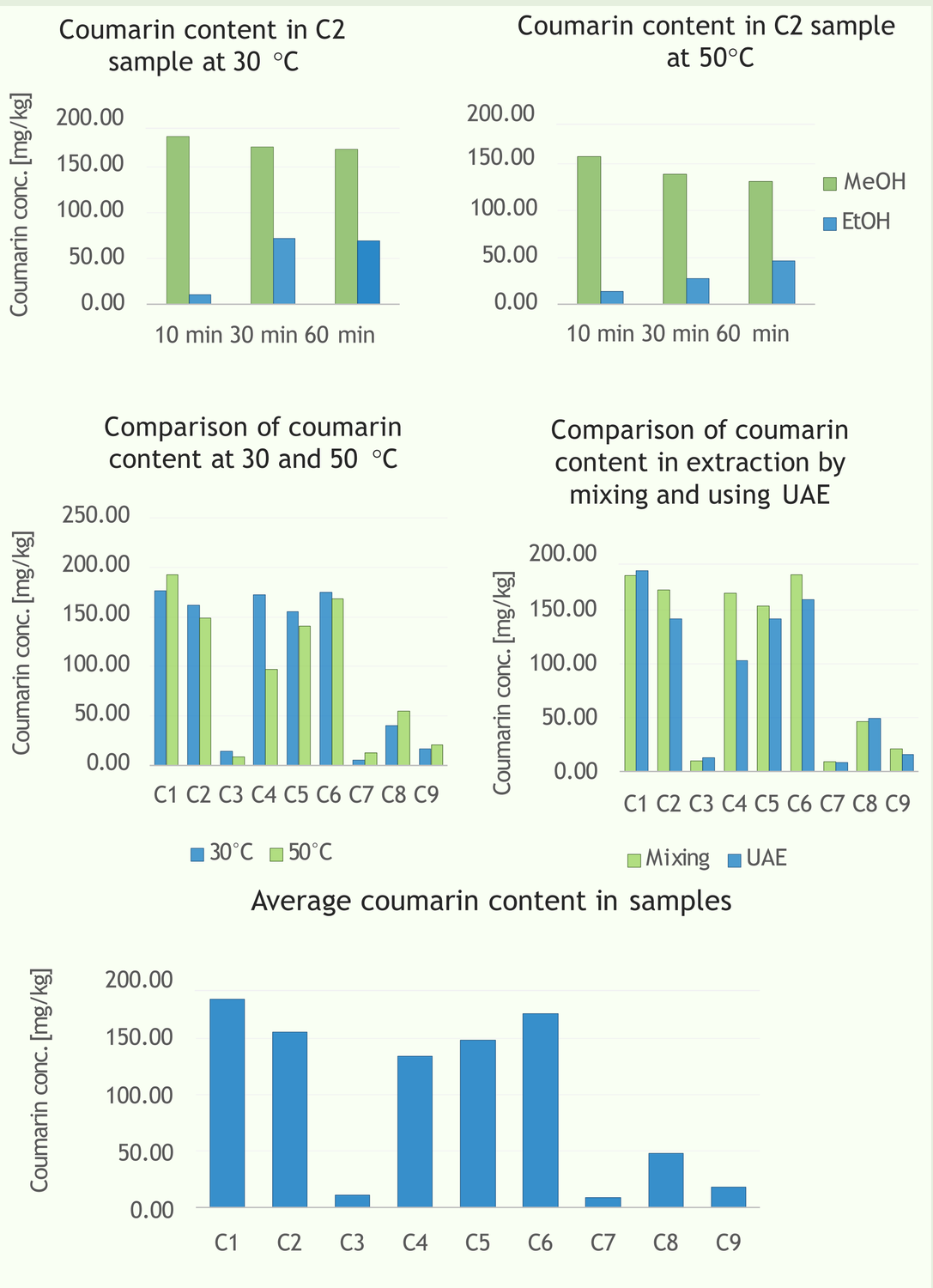

Fig. 1. Graphic representation of coumarin concentration depending on time, temperature and type of extraction (top) and average coumarin content in samples (bottom).