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Original Article

Antioxidant activity and calcium binding of isomeric hydroxybenzoates

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ABSTRACT

The association constant for calcium binding to hydroxybenzoates in aqueous 0.16 M NaCl at 25 °C was found electrochemically to have the value $K_{ass} = 280$ mol L^{-1} with $\Delta H^{o} = -51$ kJ mol^{-1}, $\Delta S^{o} = -122$ J mol^{-1} K^{-1} for the 2-isomer (salicylate), $K_{ass} = 7$ mol L^{-1} with $\Delta H^{o} = -39$ kJ mol^{-1}, $\Delta S^{o} = -116$ J mol^{-1} K^{-1} for the 3-isomer, and $K_{ass} = 8$ mol L^{-1} with $\Delta H^{o} = -51$ kJ mol^{-1}, $\Delta S^{o} = -155$ J mol^{-1} K^{-1} for the 4-isomer. The 3- and 4-isomers were found more efficient as antioxidants than the 2-isomer in decreasing oxygen consumption rate in a peroxidating methyl linoleate emulsion and less sensitive to presence of calcium. All isomers were found prooxidative for iron-catalyzed initiation of oxidation due to enhanced radical formation as shown by electron spin resonance spectroscopy. Calcium salicylate was found to have low solubility with a solubility product $K_{sp} = 4.49 \cdot 10^{-6}$ based on activity with $\Delta H^{o} = 67$ kJ mol^{-1}, $\Delta S^{o} = 123$ J mol^{-1} K^{-1} for dissolution in water, when corrected for the strong complex formation. Calcium in food and beverages may thus lower antioxidant activity of plant phenols through complexation or by precipitation.

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1. Introduction

Plant phenols are important nutrients and contribute to the health of fruit and vegetables and of beverage like coffee and tea [1–4]. Plant phenols are also important for the oxidative stability of many processed foods, as they are radical scavengers, absorbers of ultraviolet light and singlet oxygen quenchers [5–7]. Plant phenols interact together with carotenoids with redox-active metal ions like iron and copper inducing free radical processes under some conditions like during food digestion in effect becoming pro-oxidative [8–10].

Plant phenols, may, however, also interact with non-redox active metals like calcium, which could modify the capacity of the plant phenols as antioxidants or hamper their absorption from food during digestion. Such interaction has, however, been little studied despite the importance of such reactions for the stability of processed foods combining milk based component and plant material. We have selected one of the simplest plant phenols, hydroxybenzoic acid, and have studied the reactions of calcium with the three possible isomers of hydroxybenzoate, including salicylate, and report the effect of calcium on hydroxybenzoates as antioxidants.

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Interaction between metal ions and antioxidants is receiving increasing attention [8]. Better methodologies for quantification of binding of metal ions to plant based antioxidants need, however, to be developed. The present study establishes such methods using a low molecular weight antioxidant in three isomeric forms combined with calcium as an important mineral nutrient.

2. Methods and materials

2.1. Materials

Calcium chloride dihydrate, sodium chloride, disodium hydrogenphosphate, sodium dihydrogenphosphate, iron(II) sulfate heptahydrate, sodium hydroxide, and ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) were obtained from Merck (Darmstadt, Germany). Hydrogen peroxide (30%, v/v), α-(4-pyridyl-N-oxide)-N-tert-butylnitrone (POBN) and ammonium purpurate 5,5′-nitrilodibarbituric acid (murexide indicator), methanol (≥99.9%, v/v) were from Sigma–Aldrich (Steinheim, Germany). Sodium 2-hydroxybenzoate, 3-hydroxybenzoic acid, sodium 4-hydroxybenzoate, calcium salicylate, linoleic acid methyl ester, ascorbic acid, polyoxyethylenesorbitan monolaurate (Tween 20), and myoglobin from horse heart (min. 90%) were from Sigma (St. Louis, MO), while ethanol (96%, v/v) was from Kemetyl A/S (Køge, Denmark). All aqueous solutions were made from purified water using a Millipore Milli-Q purification system (Milli-Q Plus, Millipore Corporation, Bedford, MA).

2.2. Potentiometric determination of free calcium and association constants

A calcium ion-sensitive electrode ISE25CA together with a reference electrode REF 251 from Radiometer, Copenhagen, Denmark was used for measuring free calcium ion concentration in the presence of the hydroxybenzoate isomers at 0.0 °C, 10.0 °C, and 25.0 °C. The electrode was calibrated with calcium standard solutions of 1.00×10^{-4} mol L^{-1}, 1.00×10^{-3} mol L^{-1}, and 1.00×10^{-2} mol L^{-1} before measurement. The standard solutions were prepared from a 1.00 mol L^{-1} stock solution of dried $CaCl_2$ with the same ionic strength as the samples. NaCl was used for adjusting the ionic strength to 0.16 in standard solutions. The free calcium concentration of samples were determined from the linear relationship, based on the Nernst equation, between electrode potential (mV) and the corresponding calibration aqueous solution pCa value ($-\log[Ca^{2+}]$) [11]. For determination of the solubility product of calcium salicylate in water, the calcium electrode was standardized using the same calcium standards but without sodium chloride addition and calcium activity calculated according to Davies equation. For both standardization methods, the calcium electrode responded according to Nernst equation. A pH meter (713 pH Meter, Metrohm, Denmark) with a glass electrode (602 Combined Metrosensor glass electrode, Metrohm, Denmark) was used for measuring pH at ionic strength of 0.160 at 10.0 °C and 25.0 °C using activity pH standards for calibration.

2.3. Oxygen consumption rate

Two hundred and fifty microliter of 28.2 mM methyl linoleate (dissolved in methanol) was mixed with 63 μL of 0.04 g mL^{-1} Tween-20 dissolved in methanol. The methanol was then removed with a stream of nitrogen, and 2.50 mL of 5.0 mM air-saturated phosphate buffer (pH = 6.8) thermostatted at 25.0 °C was subsequently added. Ten microliter samples with a concentration of 0.00100 mol L^{-1} of the hydroxybenzoate isomers with or without 0.0100 mol L^{-1} calcium chloride were added. Twenty-five microliter of 0.20 mM myoglobin aqueous solution was added to the samples for initiating the oxidation. The mixed samples were injected into a thermostatted (25.0 °C) 70 μL measuring cell (IKA-Labortechnik, Staufen, Germany) with no headspace. The Micro-respiration system–MRch System from Unisense (Århus, Denmark) was used to determine the oxygen consumption rate in the samples. A Clark electrode connected to a multichannel analyzer ReadOx-4H (Sable Systems, Henderson, NEV, USA) was used to measure the relative oxygen concentration of the samples in the measuring cells and data were recorded for 10 min at 10 s intervals. Before testing any samples, deoxygenated ascorbic acid mixed with sodium hydroxide corresponding to 0% oxygen and air-saturated phosphate buffer (100% oxygen corresponding to $[O_2]_{initial} = 2.6 \times 10^{-4}$ mol L^{-1}) thermostatted at 25.0 °C were used for electrode calibration [12].

The oxygen consumption rate V (O_2) in μmol l^{-1} s^{-1} was calculated from:

$$V(O_2) = -\text{slope}\,[O_2]_{initial} \times 10^6/100 \quad (1)$$

The oxygen consumption rate V (O_2) was calculated based on the plot of oxygen percentage vs. time. The linear region of the curve (from 80% to 40%) was used to calculate the slope using linear regression analysis (% O_2 s^{-1}) [13]. The antioxidative activity index value was used to compare the effect of the three hydroxybenzoate each with and without calcium addition on the rate of oxygen consumption:

$$\text{Antioxidative index} = \frac{\text{Oxygen consumption rate with antioxidant}}{\text{Oxygen consumption rate without antioxidant}} \quad (2)$$

2.4. Fenton reaction with ESR detection of POBN spin adducts

A Miniscope Ms 200 Electron Spin Resonance (ESR) Spectrophotometer from Magnettech GmbH (Berlin, Germany) was calibrated with 2.0 mL POBN (3.2 M) in 1.0 M aqueous ethanol solution. Then, 2.0 mL POBN (3.2 M) in 1.0 M aqueous ethanol solution was added into the tube followed by addition of 10 μL

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