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Thermal Degradation of Onion Quercetin Glucosides under Roasting Conditions

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Flavonoids are an important constituent of the human diet. In recent years, they have gained much attention due to their physiological properties, leading to an enormous increase in research on cancer prevention and reduction of cardiovascular diseases. Unfortunately, there is limited information about the fate of flavonoid glycosides during thermal treatment such as cooking, frying, roasting, etc. Such processing techniques may have an impact on the flavonoid structure, resulting in changes of the bioavailability and activity of the flavonoids. In this study, the stability of selected model and onion quercetin glycosides under roasting conditions (180 °C) was determined. The influence of the kind and position of the sugar moiety was investigated. As onions contain large amounts of quercetin glycosides and are often subject to thermal processes in food production, their major glycosides were isolated using counter current chromatography and roasted. The thermal treatment led to a degradation of the quercetin glycosides. The main product is the aglycone quercetin, which remained stable during further roasting. During the roasting process of the quercetin diglucoside isolated from onion, the formation of a monoglycoside as an intermediate product was observed. This underlined that the stability of the glycosides is dependent on the kind and position of the sugar moiety.

KEYWORDS: Flavonoids; quercetin glycosides; thermal food processing; onions; thermal stability

INTRODUCTION

Flavonoids are an important constituent of the human diet. In recent years, they have gained much attention due to their antioxidative, antibacterial, and anticarcinogenic properties, which led to an enormous increase in research on cancer prevention and reduction of cardiovascular diseases (*1*). Flavonols especially are regarded as good antioxidants (*2*) and anticarcinogenic agents (*3*), but it is important to know the dependencies of structure−activity relationships and their influence on physiological action. From a nutritional point of view, bioavailability is the most important question when evaluating physiological effects. In recent years, many studies regarding this subject have been performed, but the bioavailability of the flavonols and their glycosides is still very controversial. However, the most important factor for bioavailability is the chemical structure of the flavonoids (*4*, *5*). Among epidemiologic studies, the biological properties of flavonoids were examined using isolated pure substances or applying flavonoid-rich food such as apples, tomatoes, onions, etc. in intervention studies (*6*, *7*). Unfortunately, such investigations do not consider the fate of flavonoid glycosides during food processing, particularly thermal treatments such as cooking, frying, roasting, etc. These processes may have an impact on the flavonoid structure, thus affecting the bioavailability and finally the biological effects. In this context, the onion is an interesting vegetable plant species due to its natural high content of phenolic compounds and its widespread popularity all over the world (*8*, *9*). In comparison to other vegetables, onions contain high levels of flavonol glycosides (mainly quercetin derivatives) (*10*, *11*), which are preferentially absorbed in humans (*12*). Furthermore, onions are subject to various domestic processing methods. They are consumed boiled in water, roasted, or even deep fried at higher temperatures. There are several reports in the literature that cooking of onions led to a decrease in total flavonol content (*11*, *13*−*16*). Far more important is the fate of the onion flavonol structures. Makris and Rossiter (*17*) showed that several new fractions were formed during the cooking of quercetin, with a major product being protocatechuic acid, a hydroxybenzoic acid. In one of our recent studies, we identified further reaction products based on oxidative degradation mechanisms catalyzed by aqueous alkaline reaction conditions (*18*). As roasting is conducted at higher temperatures under non-aqueous conditions without catalysis of alkali, the question remains if degradation also takes place. Therefore, the aim of the present study was to determine the stability of selected model quercetin glycosides (isoquercitrin, quercitrin, hyperoside, rutin, and spiraeoside) under roasting conditions (180 °C). The influence of the kind and the position of the sugar moiety was investigated. As onions contain large amounts of quercetin

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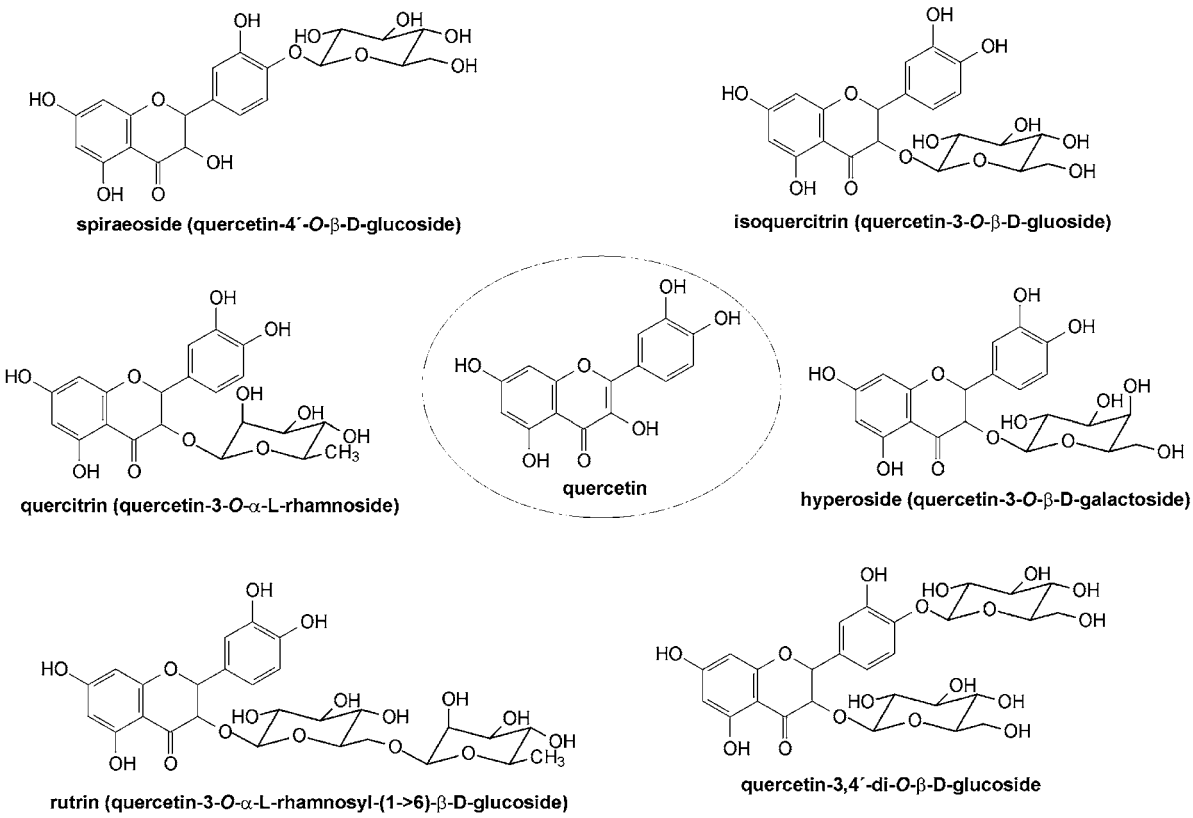

Figure 1. Chemical structures of quercetin and derivatives investigated.

glycosides and are often subject to thermal processes in food production, their major glycosides were either isolated or the whole onion was used for roasting.

MATERIALS AND METHODS

Materials. Quercetin and quercetin-3-*O*-rutinoside (rutin) were obtained from Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany. Quercetin-3-*O*-glucoside (isoquercitrin), quercetin-3-*O*-rhamnoside (quercitrin), and quercetin-3-*O*-galactoside (hyperoside) were from Extrasynthese SA, Genay, France. The purity was checked by HPLC analysis and was >97% for each compound. Quercetin-4′-*O*-monoglucoside (spiraeoside) and quercetin-3,4′-*O*-diglucoside were isolated from onions as described next. Onions were purchased from a local supermarket (Reichelt, Berlin, Germany). All the structures investigated are shown in **Figure 1**. HPLC solvents were purchased from Roth (Karlsruhe, Germany) and were of HPLC grade quality.

Isolation of the Quercetin-4′-*O*-monoglucoside and Quercetin-3,4′-*O*-diglucoside from Onions (*Allium cepa* L.). Prior to the extraction, the onions were frozen, lyophilized, and powdered. Samples were extracted as follows: 50 g of lyophilized onion powder was stirred in 500 mL of aqueous methanol (70%) for 30 min. The mixture was filtered, and the supernatant was reduced to dryness in vacuo. The dried extract was further purified on column chromatography using polyamide as a sorbent. After removing sugars and other soluble compounds by washing with warm water (50 °C), elution was performed with methanol/water/acetic acid (90:5:5, v/v). A solution of the partially purified phenolic extract in the mobile phase was applied to counter current chromatography (CCC). The CCC instrument (self-made) was equipped with a 260 mL multilayer coil column made of a 1.6 mm i.d. PTFE tubing. The mobile phase was delivered with a K-120 HPLC pump (Knauer GmbH, Berlin, Germany). A 10 mL injection loop was used for the injection of samples. The effluent was monitored at 280 nm by a LKB Uvicord SD−-UV detector (Pharmacia, Freiburg, Germany) and collected with a fraction collector.

A two phase solvent system, ethyl acetate/butanol/water (2:1:4, v/v), was used in the present study. The solvent mixture was thoroughly equilibrated in a separator funnel at room temperature, and the two phases were separated shortly before use. In CCC separation, the coil column was first entirely filled with the upper phase of the solvent system, and then the apparatus was set into rotation (800 rpm), while the lower phase was pumped into the column at a flow rate of 1.2 mL/min. After the mobile phase front emerged and hydrodynamic equilibrium was established in the column, the sample solution containing 200 mg of the partially purified extract was injected through the injection valve. The collected fractions were analyzed with HPLC-DAD and combined when sharing the same content. The purified compounds (quercetin-4′-*O*-monoglucoside and quercetin-3,4′-*O*-diglucoside) were identified with LC-MS^n and by comparing their ^{1}H and ^{13}C NMR data to the literature (*19*).

Analysis of the Flavonol Glycosides using HPLC-DAD. The Agilent HPLC-System consisted of a quaternary pump (1050 series), autosampler (1050 series), and a DAD (1100 series). A gradient elution based on Roesch et al. (*20*) using acetonitrile and acetic acid was carried out on a 250 mm × 4.6 mm i.d., 5 μm, Fluofix 120E column (Wako Pure Chemical Industries, Osaka, Japan) connected to a 10 mm × 4.6 mm i.d. guard column of the same material. Gradient elution was performed as follows: 0% B (5 min); 0−4% B in 4 min; 4−2% B in 1 min; 2−4% B in 5 min; 4−8% B in 15 min; 8−22% B in 15 min; 22−28% B in 5 min; 28% B (5 min); 28−45% B in 10 min; and 45−0% B in 1 min; all at a flow rate of 1.0 mL/min and a column temperature of 30 °C. The detection was performed simultaneously at 325, 350, and 280 nm. Spectra were recorded from 200 to 500 nm. For the analysis of whole onions, 2.5 g of lyophilized onions was extracted with 50 mL of aqueous methanol (70%) for 30 min under continuous stirring. Following filtration, 4 mL of the filtrate was diluted with the same amount of water and then loaded onto a polyamide (500 mg) solid phase extraction column. The column was washed with 10 mL of water to remove sugars and further water soluble compounds. The flavonol glycosides were eluted with 10 mL of a methanol/water/acetic acid mixture (90:5:5, v/v). This dilution was used for the HPLC-DAD analysis.

Analysis of the Degradation Products using HPLC-DAD-ESI-MS^n. ESI mass spectra of the samples were recorded using an Agilent 1100 series LC-MSD trap controlled by LC-MSD software (version 4.1). The chromatographic conditions were as described previously.

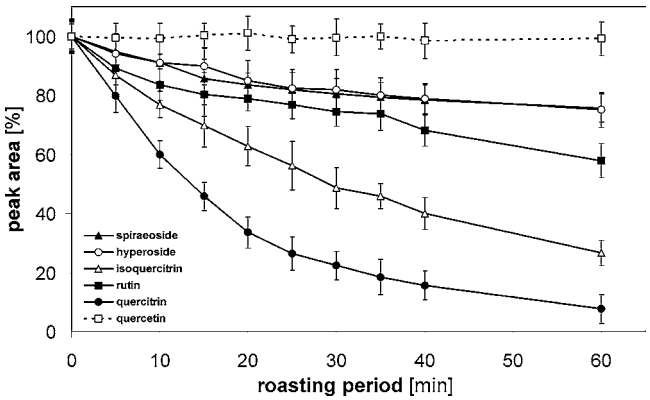

Figure 2. Degradation of selected quercetin glycosides during roasting conditions (dry roasting at 180 °C).

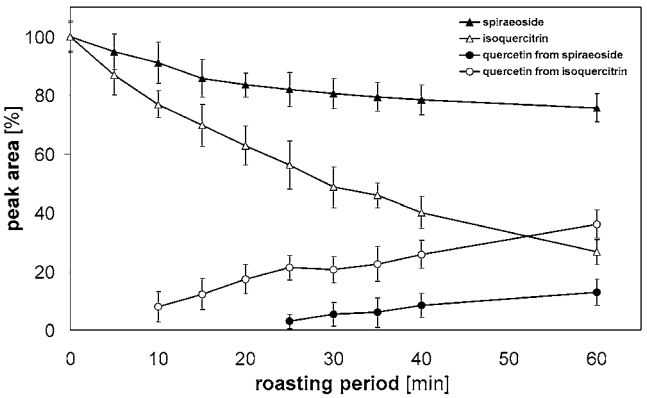

Figure 3. Formation of quercetin resulting from the degradation of spiraeoside and isoquercitrin.

The mass analyzer was set to negative mode. After detection by DAD, the flow was split, and 0.35 mL/min was subjected to ESI-MS analysis. Helium was used as the drying gas and nitrogen as the nebulizer gas. The spray shield temperature was 325 °C. A segment program using different mass ranges and averages for defined retention times (*m*/*z* 50−200 and *m*/*z* 50−900) was applied. MS^n spectra of the ions of interest were recorded using the AUTO-MS^n mode of the LC-MSD software. In this mode, the ion is separated, using smart parameter setting (SPS), and afterwards fragmented. To achieve high intensity of the product ion, the fragmentor voltage was ramped between 0.5 and 1.5 V, and an optimum was automatically selected (generally, the voltage was 1 V).

Roasting. For the roasting experiments, 1 mL of a 1 mM methanolic flavonol solution was dried under nitrogen. The roasting was carried out in glass ampoules at 180 °C in a behrotest ET1 thermoblock (Behr Labortechnik, Germany). After the roasting, process samples were redissolved and used for HPLC analysis. A total of 2.5 g of lyophilized onions was also roasted in ampoules at 180 °C, and the flavonols were analyzed as described previously.

Statistical Analysis. The roasting was repeated 4 times, and the standard deviation was calculated. A maximum of ±5% standard deviation from the averaged values was generally obtained. The averaged values along with standard deviations are documented in the respective figures.

RESULTS AND DISCUSSION

Thermal Degradation of Model Quercetin Monoglycosides. The influence of roasting conditions on flavonol glycoside degradation was investigated during a high temperature heat treatment of model substances. First of all, in the case of quercetin, the aglycone, heat treatment over 60 min at 180 °C did not show any significant degradation (**Figure 2**). In contrast, the quercetin glycosides were strongly degraded at 180 °C under nonaqueous conditions (**Figure 2**). Even after a few minutes, all glycosides showed a loss of up to 20% of the starting concentration. Quercitrin (quercetin-3-*O*-rhamnoside) especially was degraded rapidly and to a major extent: after 60 min, only 8% was left, implying that the degradation depends on the structure of the glycosides, as well as on the roasting temperature. With higher temperatures, the breakdown of the flavonol glycosides was faster (data not shown). During the roasting process, the major degradation product was identified as quercetin using HPLC-DAD-MS^n (**Figure 3**). It can be concluded that roasting of quercetin glycosides led to deglycosylation and formation of the aglycone. As mentioned previously, quercetin is not sensitive to degradation under such conditions and therefore has to be regarded as a stable end product. During cooking using aqueous conditions at around 100 °C, it was observed that quercetin was degraded to several products. Glycosides also showed an intensive breakdown but did not lead to the aglycone (*17*, *18*).

Influence of the Sugar Moiety on the Degradation. The results of the roasting experiments revealed that the sugar moiety attached to the flavonol aglycone had an influence on the degradation kinetics. When roasting several flavonol 3-*O*-glycosides, only differing in the glycoside moiety, the 3-*O*-galactoside (hyperoside) was the most stable. After 60 min of roasting, 25% of the hyperoside was degraded (**Figure 2**). The stability of the quercetin glycosides against thermal treatment under such conditions followed the order: 3-*O*-galactoside (hyperoside) > 3-*O*-rutinoside (rutin) > 3-*O*-glucoside (isoquercitrin) > 3-*O*-rhamnoside (quercitrin) (**Figure 2**). Isoquercitrin and spiraeoside carry the same sugar moiety but at different positions (isoquercitrin = 3-*O*-glucoside and spiraeoside = 4′-*O*-glucoside). During roasting, the sugar attached to the C-ring of the flavan skeleton (3-*O*-position) was more susceptible for the deglycosylation than the B-ring attachment (4′-*O*-position) (**Figure 3**). This was also underlined by the comparatively higher formation of the degradation product quercetin (**Figure 3**).

Thermal Degradation of Quercetin Diglycosides. The quercetin content of commercial onions (*A. cepa* L.) is mainly represented by quercetin-4′-*O*-monoglucoside and quercetin-3,4′-*O*-diglucoside. In spite of the fact that 20 or more flavonols are detectable in onions, quercetin-4′-*O*-monoglucoside and quercetin-3,4′-*O*-diglucoside make up to 80% of the total flavonoid fraction, whereas quercetin-3,4′-*O*-diglucoside is by far the major flavonoid. Depending on the onion variety, the quercetin-3,4′-*O*-diglucoside content is between 1052 and 1375 mg/kg fresh weight according to the literature (*21*, *22*).

At roasting temperatures, quercetin-3,4′-*O*-diglucoside was also degraded. Again quercetin, the aglycone, was identified as the major end product (**Figure 4A**). After 15 min of the reaction, only 13% of quercetin-3,4′-*O*-diglucoside (starting concentration 1 mM) were left. Quercetin increased steadily (after 15 min: approximately 0.3 mM). In contrast to the model monoglucosides, a second significant reaction product, prior to the formation of quercetin, was observed. This product appeared after 2 min of the reaction, whereas quercetin was detectable only after 5 min of the roasting period (**Figure 4A**). Mass spectrometric data and identification with an authentic standard revealed that this substance was quercetin-4′-*O*-monoglucoside. Thus, comparable to the degradation mechanism of the monoglycosides, a deglycosylation of the diglucoside occurs, which led to an intermediary monoglucoside, prior to the formation of the respective aglycone. However, quercetin-3-*O*-monoglucoside was not found. Thus, confirming the results of the model

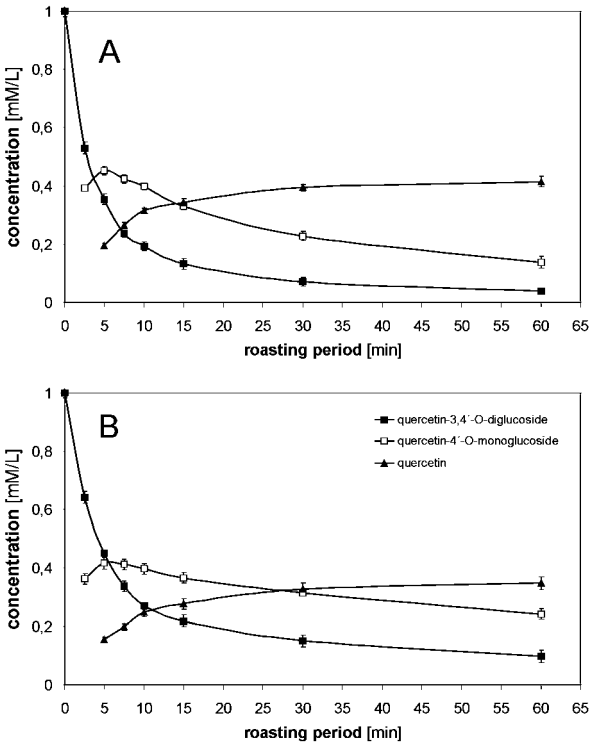

Figure 4. Degradation of quercetin-3,4′-*O*-diglucoside. (**A**) Roasting with free exposure to air and (B) roasting under nitrogen atmosphere.

monoglucoside roasting, the 4′-*O*-position had a higher stability against deglucosilation than 3-*O*-position. Besides the already mentioned parameters such as roasting temperature, period, and sugar moiety, a further influencing variable was revealed during the roasting of quercetin-3,4′-*O*-diglucoside under oxidative conditions. When the ampoules were flushed with gaseous nitrogen instead of free exposure to air, the results were markedly influenced (**Figure 4B**). The second step (breakdown of the monoglucoside) was much slower (**Figure 4B**), illustrating that besides the differences in the stability of the glycosidic bonds, oxidative effects might have played a role during the deglycosylation process. It could be assumed that the formation of the monoglycoside and the corresponding aglycone was a thermohydrolysis. Whether the cleavage proceeds via a glycosyl cation and the formation of 1,6-anhydrosugars cannot be determined at present (*23*).

In a first approach, rutin, which is also very common in all kinds of food (e.g., buckwheat (*24*) and tomatoes (*25*)), was considered as a quercetin monoglycoside (quercetin-3-*O*-rutinoside), although it is really a diglycoside. The sugar moieties were not attached to different positions of the flavan skeleton but bound as a disaccharide to the 3-*O*-position (3-*O*-rutinoside = 3-*O*-rhamnosyl-(1->6)-glucoside). Nevertheless, rutin was degraded rapidly during roasting. After 60 min, only 58% of the original rutin content was still present (**Figure 2**), and the major end product was quercetin. In contrast to the other monoglycosides, a further deglucosilation product was formed. This second product showed a *m*/*z* value of 463 and was further identified on the basis of its retention time, UV spectrum, and co-chromatography with an authentic standard as quercetin-3-glucoside. Comparable to the reaction mechanism of the real diglycoside quercetin-3,4′-*O*-diglucoside, the monoglycoside served as an intermediate prior to the formation of the quercetin.

Thermal Degradation of Onion Quercetin-3,4′-*O*-diglucoside and Quercetin-4′-*O*-monoglucoside in Different Mixtures. In onions (*A. cepa* L.), the ratio between quercetin-3,4′-*O*-diglucoside and quercetin-4′-*O*-monoglucoside is around 3:1 according to Price and Rhodes (*22*). To investigate if changes in the original profile affected thermal stability of the quercetin glycosides, three different ratios of quercetin-3,4′-*O*-diglucoside and quercetin-4′-*O*-monoglucoside (3:1; 1:1; and 1:3) were roasted (**Figure 5A**−**C**). As mentioned previously, roasting of quercetin-3,4′-*O*-diglucoside led to the formation of quercetin-4′-*O*-monoglucoside, which was further converted into quercetin. When roasting a mixture consisting of comparatively high amounts of quercetin-4′-*O*-monoglucoside and only a little of quercetin-3,4′-*O*-diglucoside, an increase in quercetin-4′-*O*-monoglucoside content was hardly noticeable (**Figure 5A**). The degradation in favor of quercetin was very fast; its formation began very early (after 2 min of the reaction), and the resulting concentration reached 0.47 mM (**Figure 5A**). With equal amounts of quercetin-3,4′-*O*-diglucoside and quercetin-4′-*O*-monoglucoside, a slight increase of quercetin-4′-*O*-monoglucoside in the first minutes of the roasting was observable. Nevertheless, the formation of quercetin occurred rapidly (**Figure 5B**), but after 30 min, its amount was comparatively lower (0.33 mM) (**Figure 5A**,**B**). When the starting quercetin-4′-*O*-monoglucoside level was only one-third of quercetin-3,4′-

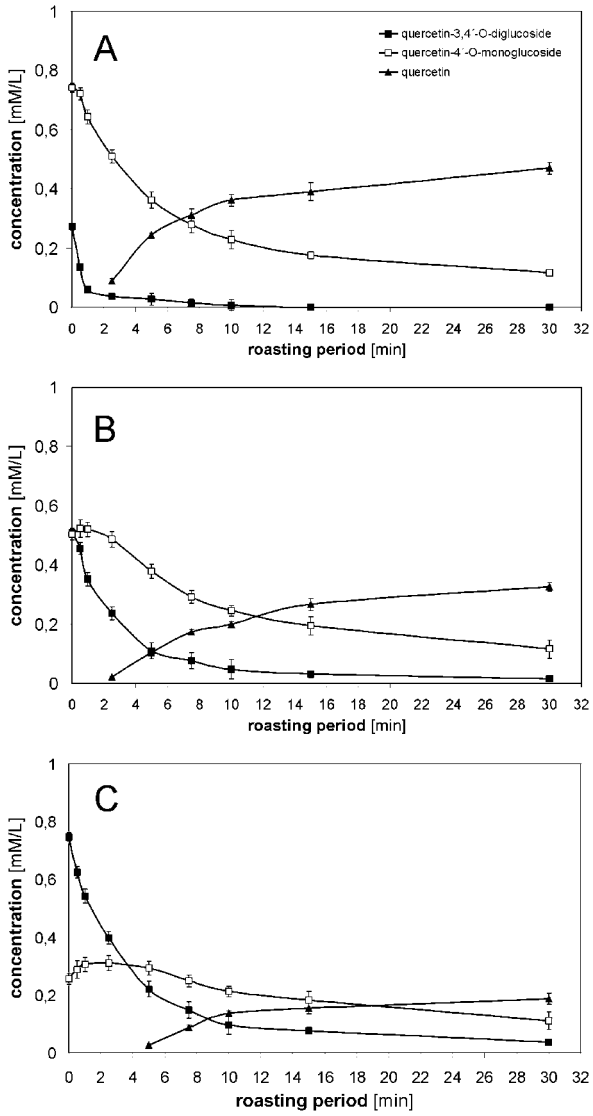

Figure 5. Roasting of different mixtures with varying amounts of quercetin-4′-*O*-monoglucoside and quercetin-3,4′-*O*-diglucoside. (**A**) 0.75 mM:0.25 mM; (**B**) 0.5 mM:0.5 mM; and (**C**) 0.25 mM:0.75 mM.

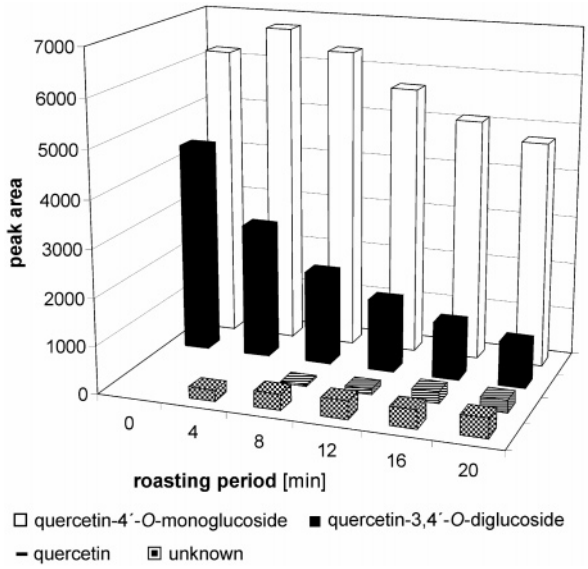

Figure 6. Roasting of an onion sample; quercetin-4′-*O*-monoglucoside and quercetin-3,4′-*O*-diglucoside.

O-diglucoside (**Figure 5C**), the results followed the (original) trend, which was shown during the single roasting of quercetin-3,4′-*O*-diglucoside: a breakdown to quercetin-4′-*O*-monoglucoside as an intermediate of the thermal induced degradation occurred, resulting in an increase of quercetin-4′-*O*-monoglucoside in the first phase of the reaction. Quercetin appeared only after a few minutes and increased steadily but did not reach the high amounts found for the other roasting mixtures (**Figure 5C**; 0.19 mM)

Thermal Degradation of Quercetin Glucosides in Onions. To investigate the influence of the food matrix, lyophilized onions were roasted under the same conditions as the model experiments. The changes in quercetin-3,4′-*O*-diglucoside, quercetin-4′-*O*-monoglucoside, and quercetin content were followed using HPLC-DAD after a clean-up step with solid phase extraction.

The results of the onion roasting are depicted in **Figure 6**. As expected from the model experiments, the quercetin-3,4′-*O*-diglucoside content decreased rapidly. In parallel, the amount of quercetin-4′-*O*-monoglucoside increased during the first minutes of the reaction. After this period, it began to break down. The occurrence of quercetin was observed from 8 min onward. Thus, formation of quercetin started comparatively later, and the resulting amount was very low. However, several other reaction products arose, with one showing strong absorbance at 350 nm. This unknown substance was neither a reaction product observed during the cooking process (*18*) nor did the mass analysis give any valuable data for proposing a structure, and further investigation is needed. Since the food matrix is often very complex, it is suggested that this new product resulted from a reaction with other food constituents. It is known from the literature that oxidation of flavonoids leads to semiquinoid intermediates and the respective quinones. These very reactive compounds are, due to their electrophilic nature, able to react with nucleophilic components of the food. Proteins especially have been shown to interact in diverse mechanisms with phenolic compounds and their respective quinones (*26*).

In our study, it was shown that during roasting conditions, quercetin-3,4′-*O*-diglucoside from onion was degraded to quercetin-4′-*O*-monoglucoside, which is more bioavailable as compared to quercetin-3,4′-*O*-diglucoside and quercetin (*6*, *7*, *27*, *28*). Degradation of rutin led to quercetin-3-*O*-monoglucoside. According to Olthof et al. (*29*), it is not important whether 3-*O*- or the 4′-*O*-glucoside is ingested, as both have the same absorption rate, but Day et al. (*30*) showed that the 4′-*O*-glucoside is more susceptible to luminal hydrolysis at the brush border membrane by the lactase phlorizin hydrolase. The aglycone is then released, which is absorbed by passive diffusion and/or may exert positive effects against mucosa as hypothesized by Murota et al. (*31*), who found higher protection capability for the 4′-*O*-glucoside.

Roasting conditions led to a thermal induced degradation of quercetin glycosides. The mechanism was a deglycosylation (thermohydrolysis) to the corresponding aglycone, where the kinetics of this reaction depended on roasting time and temperature. In the case of quercetin diglycosides, the aglycone was also formed but via a monoglycosidic intermediate, which underlines the importance of the kind and position of the sugar moiety. The product pattern, resulting from thermal treatment at high temperatures under nonaqueous conditions (roasting), was quite different as compared to the cooking process, where flavonol glycosides showed several reaction products. None of them were identified as the aglycone (*18*).

Thermal processes are often assessed as critical in food production (e.g., formation of acrylamide and loss of vitamins). Here, it seems that the roasting of the flavonol glycosides led to beneficial effects. As compared to the compounds predominantly present in onions, the flavonol diglycosides, the more bioavailable monoglycosides and aglycones were formed.

As the amount of the onion quercetin glucosides depends on onion variety and/or environmental parameters (*32*), it may be possible to affect their concentration in onions or other flavonol-rich plants by applying selected crop production techniques to create specific profiles of the flavonol glycosides with a different thermal stability and physiological bioavailability.

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