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INHIBITORY EFFECT AND PRIMARY MECHANISM OF PROANTHOCYANIDINS FROM GRAPE SEEDS AGAINST ACRYLAMIDE FORMATION IN A MAILLARD REACTION MODEL SYSTEM

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Abstract

Acrylamide, a potential health hazard with carcinogenic risk, is formed during frying or baking carbohydrate-rich foods such as potatoes and cereal products. Addition of phytochemicals during food processing may be a feasible way to reduction of acrylamide formation in food processing. Proanthocyanidins from grape seeds (PGS) consist of monomeric flavan-3-ol units (the degree of polymerization DP = 2-10, sometimes > 10-25) which are mainly linked through C4 → C8 or C4 → C6 bonds. We demonstrated that a suitable concentration of PGS could cause a significant reduction of acrylamide formation in an asparagine-glucose Maillard reaction model system at pH 6.8. The presence of PGS substantially mitigated the extent of Maillard browning. Possible inhibitory pathways and primary mechanism of PGS against acrylamide formation is discussed. PGS, a kind of condensed tannins, could precipitate amino acids through complexation, thus possibly making asparagine less available for the corresponding Maillard reaction so as to reduce acrylamide formation.

Key words*: acrylamide, grape, proanthocyanidin, Maillard reaction, asparagine-glucose*

INTRODUCTION

Acrylamide is formed during frying or baking carbohydrate-rich foods such as potatoes and cereal products (Mottram and Wedzicha, 2002). It is a potential health hazard with carcinogenic risk. This issue has raised global concerns and led to extensive studies in this field (Friedman and Levin, 2008). Many studies have shown that addition of phytochemicals during food processing may be a new feasible way for reduction of acrylamide in fried and baked carbohydrate-rich foods (Zhang et al., 2009; Zhu et al., 2009). Proanthocyanidins from grape seeds (PGS) consist of monomeric flavan-3-ol units (the degree of polymerization DP = 2-10, sometimes > 10-25) which are mainly linked through C4 → C8 or C4 → C6 bonds (Fig. 1) and possess a wide range of biological activities (Xia et al., 2010). The aims of this study were to investigate the reducing effect of PGS against acrylamide formation in a Maillard reaction model system, and to elucidate its primary mechanism of action.

MATERIALS AND METHODS

The effect of different concentrations (0.001, 0.01, 0.05, 0.1, 0.5 and 1.0%; 0% as control) of proanthocyanidins isolated and purified from grape seeds (PGS > 90%) against acrylamide formation was evaluated in an equimolar asparagine-glucose model system at pH 6.8 (phosphate buffer) (Zhu et al., 2009). The relevant Maillard reactions were conducted in an oven at 120-220°C for 10-25 min.
HPLC-DAD (HP 1100 series, Germany) and LC-PDA-APCI-MS (LC-MS-2010A system, Shimadzu, Japan) were used for quantifying acrylamide and monitoring important intermediates produced via Maillard reaction in the tested samples according to the previous methods (Zhu et al., 2009; Zhu et al., 2010; Channell et al., 2008). The color changes (L^*, a^*, and b^*) after Maillard reactions of the asparagine-glucose samples added with PGS were monitored using a colorimeter (Minolta Chroma Meter CR-300, Japan).

RESULTS AND DISCUSSIONS

Figure 2 shows that PGS could significantly reduce acrylamide formation in a dose-dependent manner, with a decrease of 23.2-58.4% acrylamide compared with control, although not in a linear manner. Surprisingly and interestingly, a significantly positive PGS-concentration-dependent relationship of acrylamide inhibitory rate occurred with the PGS treatment range of 0.001-0.1%, but a slightly negative relationship with the PGS treatment range of 0.1-1.0%. In comparison with control (0% of PGS), 0.1% PGS treatment had the highest inhibitory rate (58.4%) against acrylamide formation.

It was also found that the addition of PGS in the model system considerably mitigated the extent of Maillard browning (Table 1). The *a** and *L** values are the most commonly used parameters to monitor browning, with a lower *a** value and a higher *L** value indicating a lower degree of browning.

Data obtained by LC-PDA-APCI-MS in the present study could be helpful for primary analysis of inhibitory mechanism of PGS against acrylamide formation in the model system. The proposed main pathways of acrylamide formation in asparagine-glucose model system via Maillard reaction are summarized in Figure 3, based on the review reports[8,9]). PGS, a kind of condensed tannins, could precipitate amino acids through complexation, thus possibly making asparagine less available for the corresponding Maillard reaction so as to reduce acrylamide formation. Other possible pathways for inhibitory effect of PGS against acrylamide formation (Figure 3): (1) PGS likely reacted directly with acrylamide precursors to generate new Maillard intermediates for changing the pathways of acrylamide formation; (2) PGS might influence and inhibit some key procedures of the Maillard reaction in Figure 2, such as the formation of Schiff base, Strecker type degradation, N-glucoside pathway and β-elimination reaction of the decarboxylated Amadori compounds.

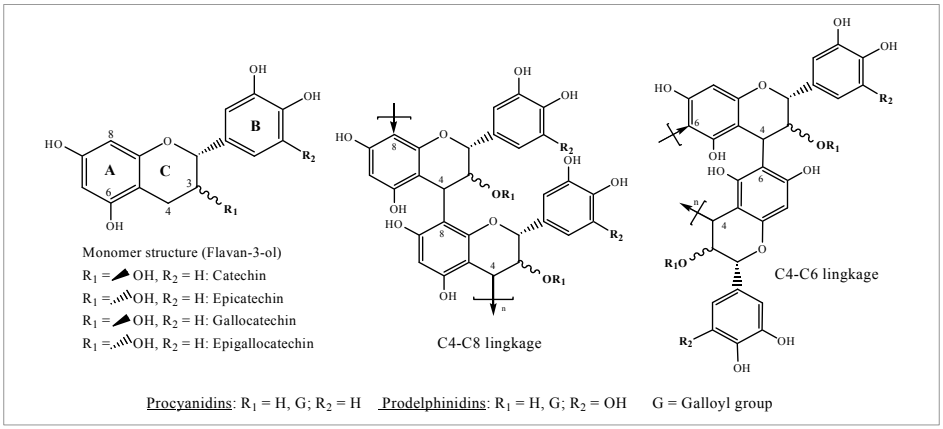

Figure 1. Basic chemical structures of proanthocyanidins (flavan-3-ol monomers and polymers) from grape seeds)

Table 1. Changes of color parameters of the asparagine-glucose samples added with different concentrations of proanthocyanidins from grape seeds (PGS) after Maillard reaction under the selected conditions

Concentration of PGS (%)	*L**	*a**	*b**
0 (control)	15.4 ±	19.3 ± 0.11	13.7 ± 0.28
0.001	17.3 ±	14.6 ± 0.26	15.6 ± 0.22
0.01	22.7 ±	11.4 ± 0.24	21.5 ± 0.18
0.05	27.5 ±	9.6 ± 0.31	24.9 ± 0.15
0.1	33.9 ±	8.1 ± 0.29	27.3 ± 0.30
0.5	30.8 ±	6.8 ± 0.38	28.1 ± 0.27
1.0	31.2 ±	6.0 ± 0.25	27.4 ± 0.32

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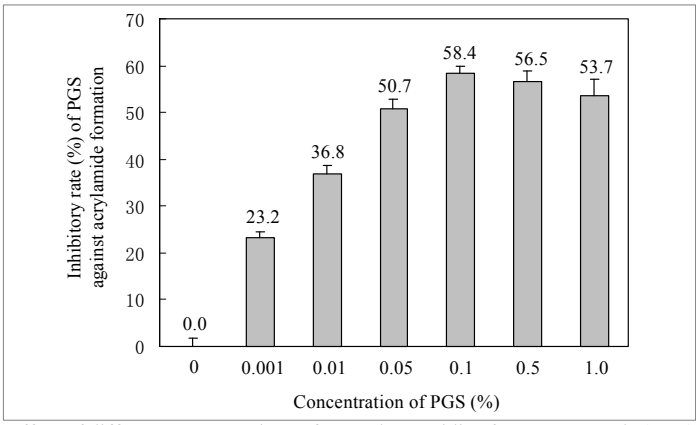

Figure 2. Inhibitory effect of different concentrations of proanthocyanidins from grape seeds (PGS) against acrylamide formation in an asparagine-glucose model system for Maillard reaction at 180°C for 20 minutes

CONCLUSIONS

Suitable concentration of PGS could cause a significant reduction of acrylamide formation in the Maillard reaction model system. The presence of PGS in the tested model system considerably mitigated the extent of Maillard browning. Possible inhibitory pathways and primary mechanism of PGS against acrylamide formation was also discussed in this study.

ACKNOWLEDGEMENTS

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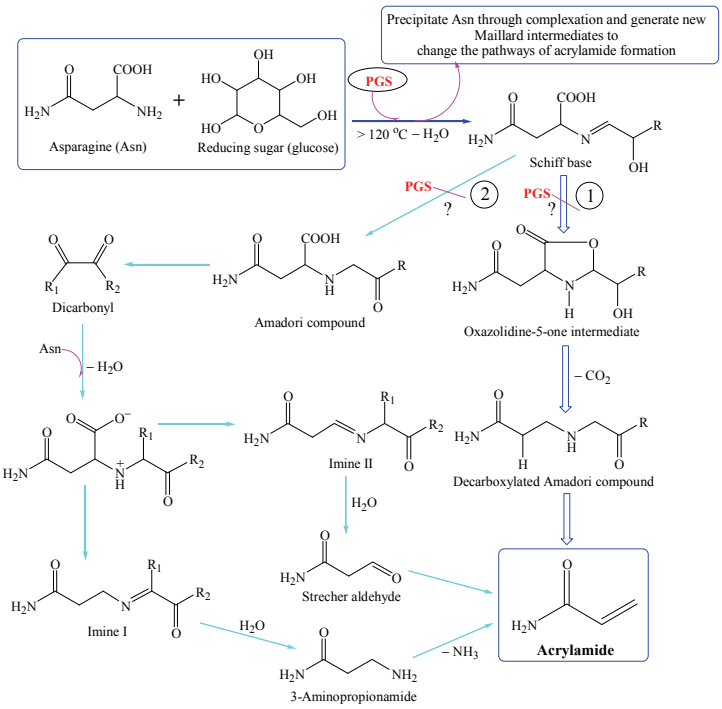

Fig. 3. The proposed main pathways of acrylamide formation in asparagine-glucose model system through Maillard reaction and the possible inhibitory mechanism of PGS against acrylamide formation

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