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Note

Vitisin-Type Pigments: Possible Novel Food Colors

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Spectral properties of different forms of several vitisin-type pigments, recently found in red wines and grapes, were studied. These orange-red tone compounds seem to be promising anthocyanin based food colors.

Key words: vitisin-type pigments, wine pigments, food colors

INTRODUCTION

There is worldwide interest in using food colorants from natural sources to replace artificial colorants.[1] Anthocyanins are the largest group of water-soluble natural pigments that have been used with some commercial success.[2] Anthocyanins are responsible for most of the red, purple, and blue colors exhibited by flowers, fruits, and other plant tissues.[3] However, they usually incur the disadvantages of color instability, spontaneous degradation and conversion to uncolored forms under heat, light, and moderate pH.[4]

Many efforts have been made to search for highly stable anthocyanins from fruit, vegetables, or ornamental plants, and to improve the stability of anthocyanins.[5] Production of anthocyanins from cell cultures has been investigated.[6] Also, there is the current medical interest in anthocyanins: for example, anthocyanins possess potent antioxidant properties.[7] The presence

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of significant amounts of anthocyanins in red grapes and wines contributes to their powerful antioxidative activity. A famous phenomenon associated with anthocyanins is the so-called »French Paradox«. Moderate consumption of red wines by the French could provide an explanation for the low cardiovascular disease mortality rate encountered in that country.[8]

Anthocyanins are important constituents of grapes and red wines. They are the main compounds involved in the color of red wine.[9] A large number of potential sources of anthocyanins have been suggested as potential food colorants. The oldest and most abundant anthocyanin extract is »enocianina« or enocyanin, produced from red grape pomace, which has found application as a general food colorant.[10] HPLC analyses of fortified red wines revealed, in small quantities, new anthocyanin-derived red pigments.[11] Another related red wine pigment has been found recently.[12]

The purpose of this study was to evaluate the spectral characteristics of the aglycones of new red wine pigments in an attempt to optimize utilization of naturally occurring colorants from grapes and wine. Calculations of electronic absorption spectra were carried out using the PPP method.[13]

VITISIN-TYPE PIGMENTS

Malvidin-type anthocyanins are the prevailing anthocyanins in red wine made from *Vitis vinifera* grapes. During the conservation and aging of red wines, formation of new pigments occurs as a result of the interaction between anthocyanins and other products extracted from grapes. If aging goes on for long periods, colored precipitates appear. Malvidin-type pigments, vitisin A and vitisin B, were found in small amounts in some red wines and at trace levels in stored grapes.[14,15] The structure of another red wine pigment has been published recently.[16] In grapes and wines, the vitisins are in the red flavylium form AH^+. Like common anthocyanins, as the pH is raised, they may form the blue-purple quinoidal-base (A-7 and/or A-4'), the colorless carbinol pseudo-base B, and the pale yellow or colorless chalcone C. The proposed structural transformations of vitisidin A (the aglycone of vitisin A),[17] which match exactly those of anthocyanins, are presented in Figure 1.

Spectral characteristics of vitisidin A, vitisidin B, and the aglycone of the related malvidin-derived wine pigment were evaluated. Structures of these pigments as well as the corresponding calculated absorption maxima in UV/VIS spectra λ_{max} (in nm) are presented in Figure 2.

All the studied pigments possess a malvidin substitution pattern. Due to substituted C-4 position, absorption maxima of their acidic AH^+ form exhibit hypsochromic spectral shifts from malvidin 3-glucoside, and thus give rise to the orange hue of red coloration. Flavylium structure AH^+ dominates to approximately pH 5, while at nearly neutral pH the other dominant form

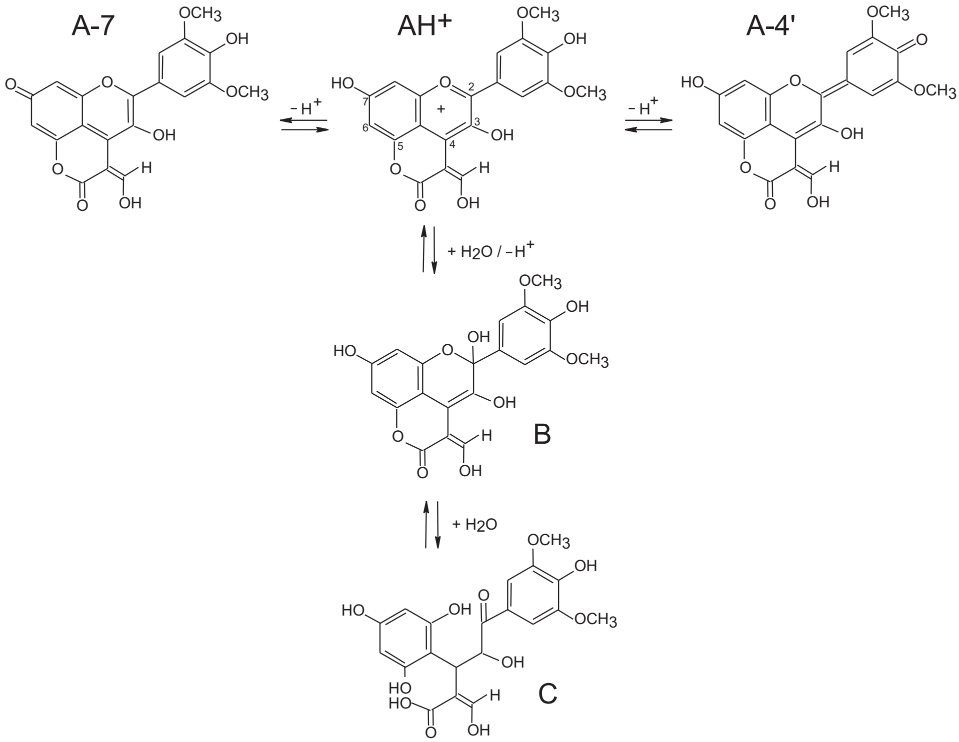
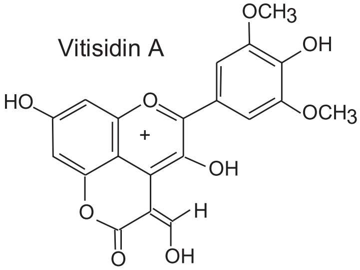
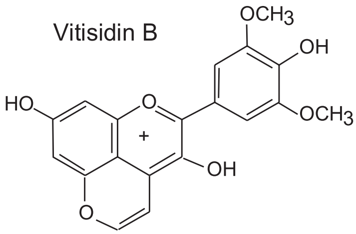
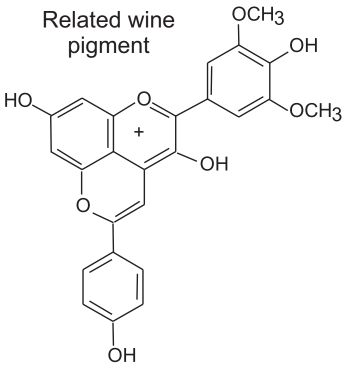


Figure 1. Proposed structural transformations of vitisidin A.

is the quinoidal-base A, which itself is bluish-red in color. As mentioned in the literature,[18] the quinoidal-base form of malvidin pigment is mainly of A-4' form. Thus, slightly acidic and neutral solutions of vitisidins should be preferably red colored.

Three decades ago it was shown that the pigments of aged red wine are more stable than the anthocyanins themselves.[19] The presence of substituent at C-5, and in particular substitution at C-4 in vitisidins, both stabilize the colored forms (AH^+ and A), *i.e.* protect the molecule from hydration, which usually leads to the colorless carbinol pseudo-base B.[20] C-4 substitution should also give rise to resistance of vitisidins to color bleaching by sulphur dioxide. Considering that SO_2 is widely used in food products, it is a desirable property. A very recent publication reported that vitisin-type pigments express much more color than the common anthocyanins.[21]

The pathway for the formation of vitisidin-type compounds seems to involve reactions between synthetic aglycones of anthocyanins or related flavylium salts with naturally occurring constituents in grapes and wines. These reactions could be guided by calculation of UV/VIS spectra of the pro-

Aglycone of anthocyanin-derived wine pigment	Electronic spectra[a]					
	AH$^+$ form		A-7 form		A-4' form	
	λ_{max}/nm	f	λ_{max}/nm	f	λ_{max}/nm	f
Vitisidin A 	509.4	0.817	563.2	0.775	558.6	1.537
	381.5	0.064	396.8	0.511	406.6	0.002
	346.6	0.515	376.9	0.142	382.8	0.033
Vitisidin B 	486.2	1.121	539.0	0.668	545.0	1.994
	380.1	0.086	419.4	0.339	401.6	0.002
	337.6	0.028	354.1	0.163	382.9	0.025
Related wine pigment 	508.0	1.273	544.2	0.648	584.3	2.207
	392.0	0.352	454.6	0.872	402.8	0.016
	351.1	0.320	346.7	0.619	399.6	0.019

[a]Calculated by PPP method.

Figure 2. Absorption spectra of the studied anthocyanin-derived wine pigments. Calculated absorption maxima in UV/VIS spectra λ_{max} (nm) and the corresponding oscillator strengths (f).

posed vitisidin-type analogue. A structure with desirable spectral properties could be consequently synthesized. It will be interesting to see if some future experimental work should support this reasoning.

CONCLUSION

Molecular features of the studied aglycones of new wine pigments, vitisidins, could overcome the well known shortcomings of anthocyanins as food colorants. Their desirable color and stability properties suggest that they may be appropriate for many food applications (as natural alternatives to artificial colorants). Further work is required to elucidate the chemical nature of the individual red wine pigments, and the mechanisms of their formation during vinification. This is of interest as a potential method for large-scale production of vitisin-type pigments.

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SAŽETAK

Pigmenti tipa vitisina: moguća nova prehrambena bojila

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Proučavane su spektralne osobine različitih oblika nekoliko pigmenata tipa vitisina, nedavno detektiranih u vinu i grožđu. Ti narančastocrveni spojevi antocijanidinske strukture mogu se pokazati potencijalno upotrebljivima kao bojila za hranu.