

Improving colorimetric properties and stability of acylated anthocyanins through UV irradiation

Yucheng Zhou, M. Monica Giusti



ABSTRACT

Anthocyanin-based food colorants are usually acylated with hydroxycinnamic acids, which occur in nature predominantly in the *trans*-configuration, with *cis*-configuration rarely found. The *trans*- and *cis*-isomers have different colorimetric properties and stability. *Trans*-isomers can isomerize to *cis* under UV irradiation in methanol.

Cis- and *trans*-isolates were extracted from American elderberry and isolated by semi-prep HPLC. 100 to 800 μ M crude extracts or purified *trans*-isolates were irradiated by UV light (254nm) in acidified water, methanol or ethanol until reaching equilibrium. The conversion rate was monitored by uHPLC. Color and spectra of UV-irradiated crude extract, *cis*- and *trans*-isomers were monitored over 72hr at pH1–9.

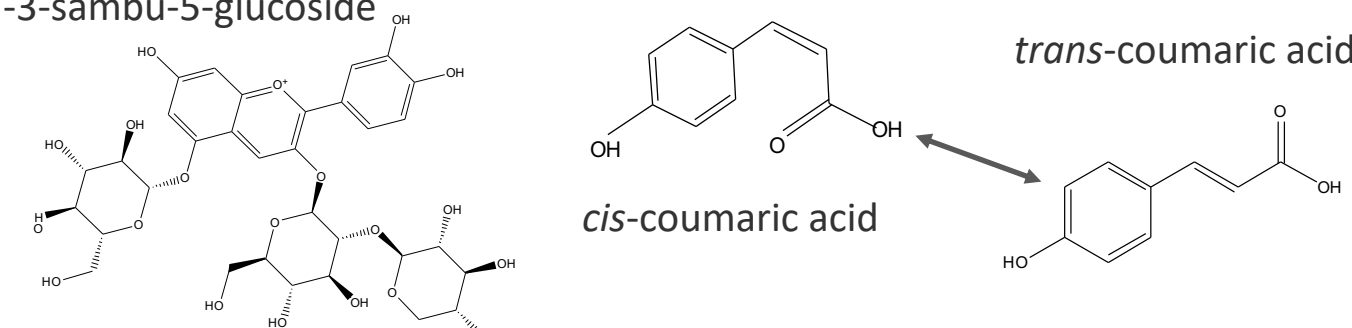
Cis-isomers were more stable, with shaper spectra, larger λ_{\max} and higher absorbance at all pH, with more color at pH4-6 and bluer hues at pH7-9. *Trans*→*cis* conversion occurred in *trans*-isolates and crude extract with similar efficiency. A plateau was reached at *trans*:*cis* ratio 5:4 in alcohol and 10:3 in water. The conversion was faster in low anthocyanin concentration, but more *cis*-isomers were produced at high anthocyanin concentration. The crude extract displayed bluer hues at pH7-9 after UV irradiation.

INTRODUCTION

American elderberries are a rich source of the acylated anthocyanin cy-3-sam-5-glu acylated with coumaric acid⁽¹⁾.

Anthocyanin acylation typically enhances its color stability due to the inter- and intra-molecular interaction⁽²⁾. The hydroxycinnamic acids are unique aromatic acyl groups: due to the existence of the double bonds in their sides chains, they have both *cis* and *trans* isomers. *P*-coumaric, caffeic, ferulic and sinapic acids are the common ones.

Cyanidin-3-sambu-5-glucoside

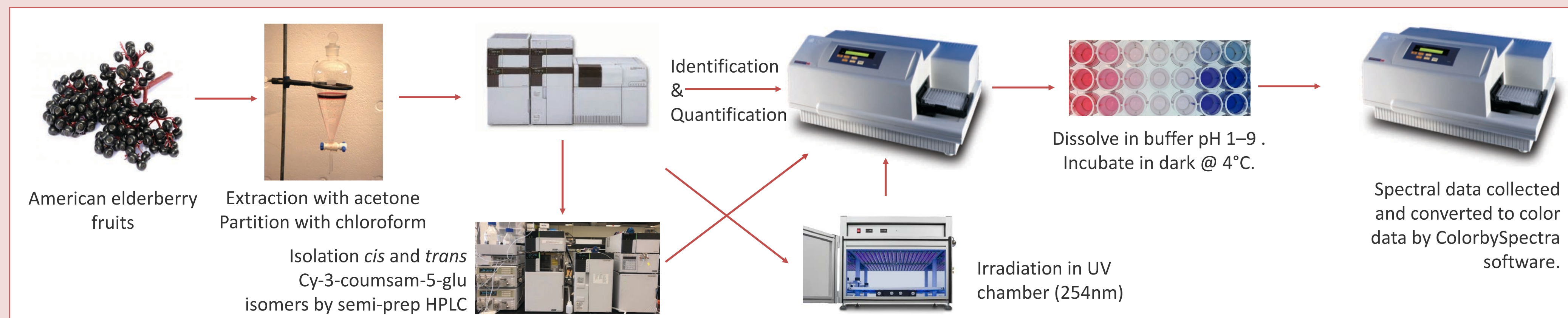


In nature the *trans* form is predominant, with very few ACNs from edible source acylated with *cis* isomers. The conversion between the two isomers rarely happens *in vivo*. Yet, the *trans*-isomers can be converted into their corresponding *cis* with artificial (UV light) irradiation or sunlight in methanolic solution *in vitro*⁽³⁾.

OBJECTIVES

Our goal was to explore the effects of coumaric acid configuration on spectral and colorimetric properties of acylated cyanidin-derivatives and determine the effects of solvent, anthocyanin purity and concentration on the UV-induced *trans*→*cis* conversion process.

MATERIALS & METHODS



RESULTS & DISCUSSIONS

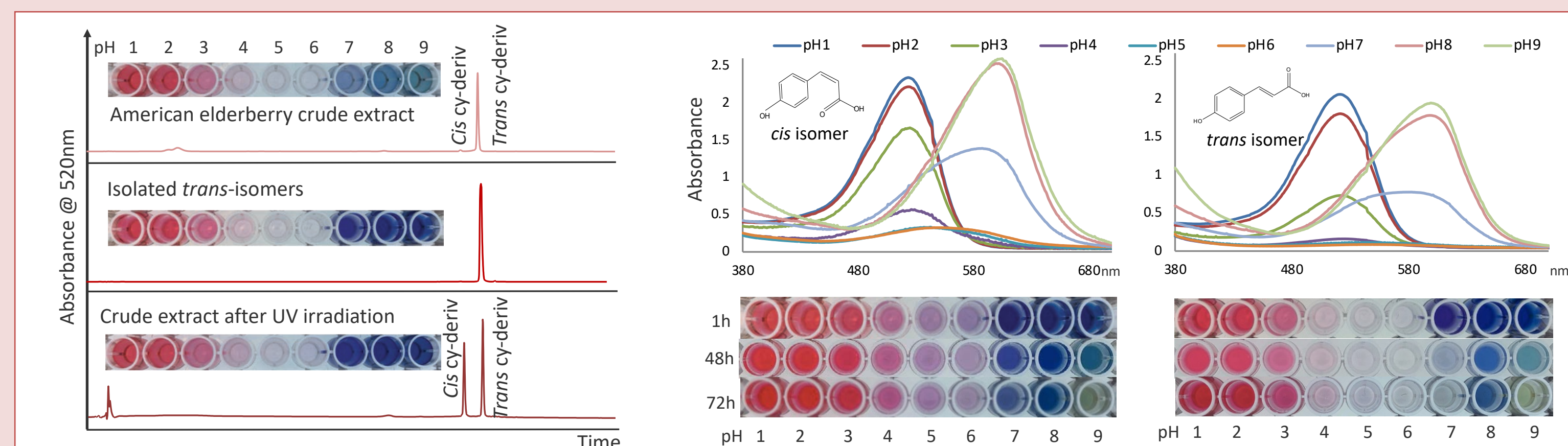


Fig 1. Chromatograms and color expression of *trans*-isomers, American elderberry crude extract before and after 12min UV irradiation.

Fig 2. Visible light spectra (1h after mixing) and color stability of isolated *cis* and *trans* isomers in pH1 – 9 buffer, samples were stored in dark at 4°C.

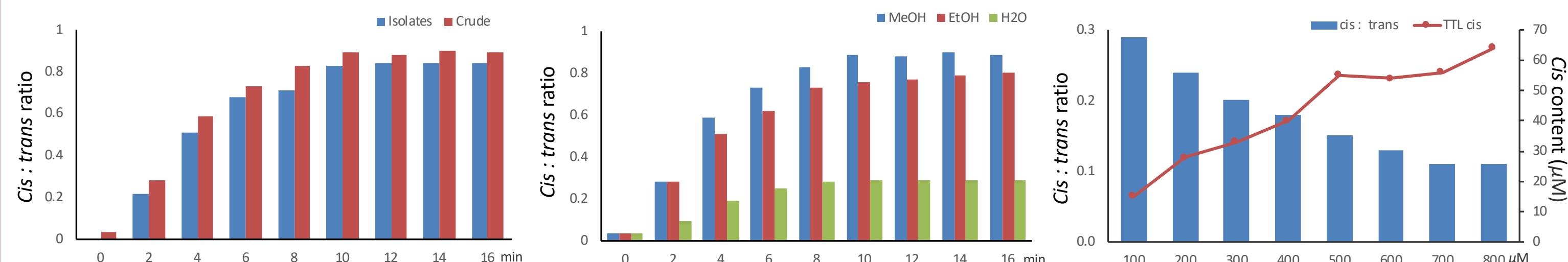


Fig 3. *Cis* : *trans* ratio of 100 μ M American elderberry crude extract or *trans*-isomers dissolved in acidic methanol during 16min UV irradiation at 254nm.

Fig 4. *Cis* : *trans* ratio of 100 μ M American elderberry crude extract dissolved in acidic methanol, ethanol or water during 16min UV irradiation at 254nm.

Fig 5. *Cis* : *trans* ratio of 100 - 800 μ M American elderberry crude extract dissolved in acidic water solution after 16min UV irradiation at 254nm.

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DISCUSSIONS

1. American elderberry contained *cis* and *trans* acylations, rare in nature (Fig 1).
2. Anthocyanin with *Cis* acylation showed higher stability, shaper spectra, larger λ_{\max} and higher absorbance at all pH than the corresponding *trans*, with bluer hues at pH 7-9 (Fig 2). Stereochemical differences of isomers may be key for color loss at pH4-6.
3. *Trans*→*cis* conversion was induced by UV irradiation at 254nm and reached equilibrium in 16min (Fig 3 – 5).
4. *Trans*→*cis* conversion happened in both elderberry crude extract and *trans*-isolates with similar efficiency (Fig 3).
5. *Trans*→*cis* conversion was more efficient in alcoholic solution (methanol or ethanol) than in the water (Fig 4).
6. *Trans*→*cis* conversion favored under low anthocyanin concentration, but the amount of *cis*-isomers produced was higher at high anthocyanin concentration (Fig 5).

CONCLUSIONS

Crude anthocyanin extracts in ethanol at low concentration irradiated by UV light (254nm) could be an efficient way to trigger *trans* → *cis* conversion of acylated anthocyanins. This novel process improved anthocyanins stability, and potentially producing promising anthocyanin-based colorants for the food industry.



THE OHIO STATE UNIVERSITY

COLLEGE OF FOOD, AGRICULTURAL,
AND ENVIRONMENTAL SCIENCES