Thermal Degradation Kinetics of Xanthophylls from Blood Orange in Real and Model Food Systems

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Blood orange juices are widely consumed in Mediterranean area. They have potential health benefits owing to their anthocyanins and carotenoids contents. While xanthophylls account for the majority of carotenoids in *Citrus*, few kinetic data on their degradation are available in literature. The major blood orange xanthophylls (cis-violaxanthin, lutein and β-cryptoxanthin (Fig. 1)) degradation kinetics were studied in real juice and in two model systems formulated to evaluate the impact of xanthophyll form (esterified or free) on their degradation and to assess the protective role of the food matrix.

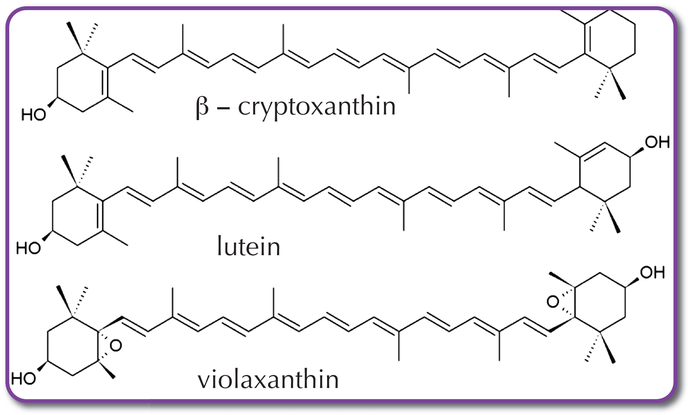

Fig. 1. Chemical structure of ß-cryptoxanthin, lutein, and cis-violaxanthin.

Materials and methods

- Sanguinelli blood oranges (*Citrus sinensis* L. Osbeck) juice from Algeria (Bejaia) was filtered and stored under nitrogen at -20°C until analysis or heat treatment (Fig. 2).
- From the juice, two model systems were formulated consisting in a) esterified or b) free xanthophyll extracts in an aqueous medium (Fig. 2).
- Heat treatments were conducted at 45, 60, 75, and 90°C.
- Xanthophylls analysis were done by HPLC using C30 column with photodiode array detector (DAD) according to Dhuique-Mayer *et al.* (2005).
- Kinetic parameters were identified by non linear regression using Matlab®.

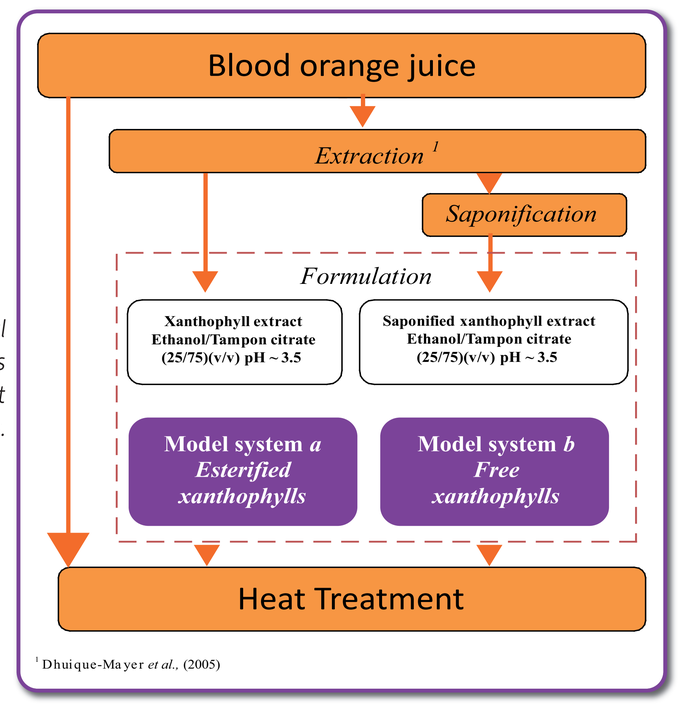

Fig. 2. Scheme of real juice and model systems preparation before heat treatments.

Results and discussion

All degradation curves were best fit by a second order model for all temperatures and all media. All xanthophylls were less degraded in real juice than in both model media (Fig. 3). The esterified forms in model a followed the same trend than in real juice. The free xanthophylls were more degraded than the esterified forms. Particularly the epoxy-xanthophyll, cis-violaxanthin disappeared totally in acidified medium. This disappearance was concomitant with a new HPLC peak apparition identified as auroxanthin (Fig. 4). This phenomenon was due to isomerisation of the 5,6-epoxy groups of cis-violaxanthin into 5,8-epoxy groups (Melendez-Martinez *et al.*, 2010).

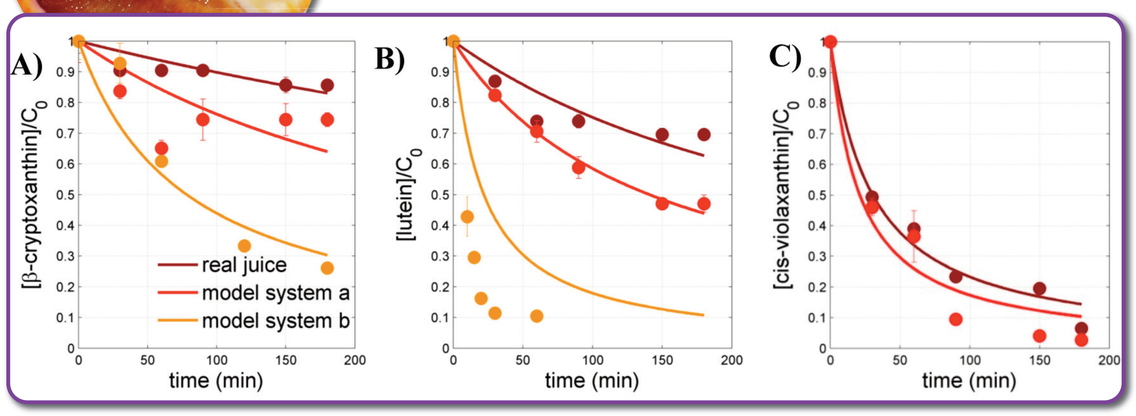

Fig. 3. Experimental concentrations (dots) during heat treatments at 75°C of A) β-cryptoxanthin, B) lutein, and C) cis-violaxanthin in real juice, model system a and system b. Error bars represent the standard deviation (n = 3) and lines represent the second order model fit.

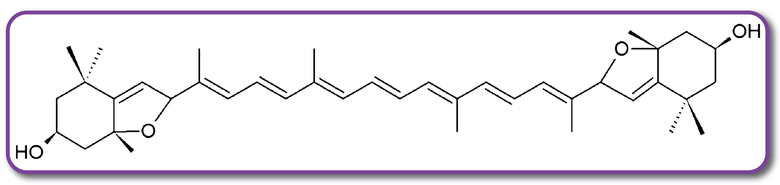

Fig. 4. Chemical structure of auroxanthin.

The rate constants obtained at four temperatures and activation energies confirmed the degradation trends. Indeed, in real juice, average degradation rates and activation energies were the lowest for the 3 xanthophylls (table I). In all media, β-cryptoxanthin was the most stable form, followed by lutein and cis-violaxanthin. In model system a, average degradation rates and activation energies exhibited a slight increase for β-cryptoxanthin and lutein and a 3-fold increase for cis-violaxanthin. In model system b, average degradation rates were much higher since they exhibited a 3 and 4-fold increase for β-cryptoxanthin and lutein while their activation energies increased by a 1.5 factor.

Table I. Kinetic parameters (activation energy and rate constant at the reference temperature of 67.5°C) of xanthophyll thermal degradation in blood orange juice and model systems a and b.

		ß-cryptoxanthin	Lutein	Cis-violaxanthin
kref ($m^3.kg^{-1}.min^{-1}$)	Real juice	2.0 ± 1.1	2.8 ± 1.7	6.2 ± 1.0
	Model system a	2.0 ± 1.2	4.2 ± 2.0	14.0 ± 1.5
	Model system b	7.5 ± 3.2	9.0 ± 2.1	-
Ea ($kJ.mol^{-1}$)	Real juice	62.3 ± 34.7	65.0 ± 21.8	58.7 ± 6.5
	Model system a	84.4 ± 33.9	88.2 ± 33.7	173 ± 12.8
	Model system b	96.0 ±24.0	98.3 ± 12.4	-

The kinetic results obtained were treated using principal component analysis (Fig. 5). Logically, rate constants of the different xanthophylls were mainly influenced by temperature (first axe F1). However, the second axe F2 discriminated two groups of xanthophylls following the nature of their oxygenation. Therefore, kinetic data enabled the discrimination of xanthoyphylls as a function of their chemical structure.

Fig. 5. Principal Component Analysis of xanthophylls degradation rate constants.

Conclusion

This work showed that free xanthophylls degraded faster than their esterified forms. Therefore, the esterification of xanthophylls with a fatty acid seemed to stabilize them. This fact is particularly obvious for the epoxy xanthophyll, cis-violaxanthin, that disappeared totally in its free form in acidic medium. Kinetic parameters also suggested that real juice may contain phytochemical compounds able to protect xanthophylls especially at high temperatures. These results will help to predict the thermal degradation of xanthophylls and determine optimal processing conditions for orange juice quality improvement.

References

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