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## How PH and redox potential can modulate color expression of yellow-orange chromophores? An analytical and electrochemical study in the colorful world of apple juices...

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HOW pH AND REDOX POTENTIAL CAN MODULATE  
COLOR EXPRESSION OF YELLOW-ORANGE CHROMOPHORES?  
AN ANALYTICAL AND ELECTROCHEMICAL STUDY IN THE COLORFUL  
WORLD OF APPLE JUICES...

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### MAIN CONCLUSION

This study compared the impact of the modulation of pH and redox potential on the chemical structures of two recently identified yellow phenolic chromophores.

### INTRODUCTION

Beverages color is generally the first criterion striking the consumer: it can initiate purchase impulse and influence subsequent sensorial perceptions<sup>1</sup>. Nowadays, French conventional apple juices and ciders cover a large range of colors, from pale yellow to orange-brown. The colored compounds are mainly formed during fruit processing by enzymatic oxidation and molecular rearrangements of the native polyphenols. Up to now, two main classes of colorants are distinguished within the identified yellow-orange compounds. First, some colorants are derived from the oxidation of dihydrochalcones like phloridzin or phloretin xyloglucoside, such as yellow POP<sub>j</sub><sup>2</sup> (Phloridzin Oxidation Product, Fig. 1a) and yellow PXGOP<sub>j</sub><sup>3</sup> (Phloretin XyloGlucoside Oxidation Product). Secondly, colorants resulting from the oxidation of flavanol monomers, especially (-)-epicatechin, are also found in apple juices. This study focused on two physicochemical parameters, the pH and the redox potential, which could modulate the color expression of two apple juice model chromophores: the POP<sub>j</sub> and a colored dehydrotricatechin.

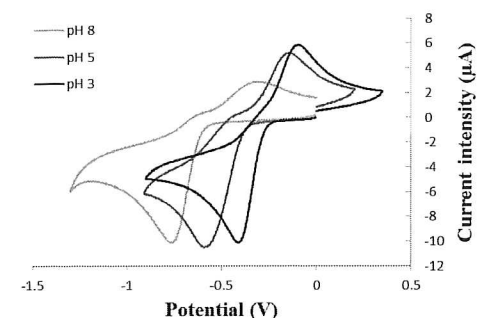
### MATERIALS AND METHODS

Both model chromophores were obtained in model media, by enzymatic incubation of the colorless precursors with an apple polyphenol oxidase extract. They were purified by semi-preparative HPLC steps. The pH effect on color was evaluated on a pH range from 2.5 to 8 (Mellvaine buffers containing 5% of methanol) by recording the UV-visible spectra of 50 µM chromophore solutions. Absorbance data were then converted to colorimetric parameters (CIE Lab/LCh space) by mathematical processing. Moreover, the reduction potentials were investigated by cyclic voltammetry studies on glassy carbon (2 mm Ø) and platinum (1 mm Ø) disk working electrodes on a dual potentio-galvanostat. The impact of reduction on color was then studied by UV-Visible spectroelectrochemistry followed by HPLC-DAD-MS analysis of the electrolyzed solution.

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### RESULTS AND DISCUSSION

The pH effect on the stability of different polyphenolic structures was often highlighted in previous studies. The pH can significantly vary according to the French cider apple varieties used to produce juices and ciders. Thus, it likely plays a role in the contrasted colors observed. A significant effect of pH was noticed on the modulation of color for both studied chromophores (Fig. 1b). However the dehydrotricatechin appeared more stable than POP<sub>j</sub>, this last exhibiting a bright yellow color at pH 3 to 5, turning clearly to orange for higher pH.



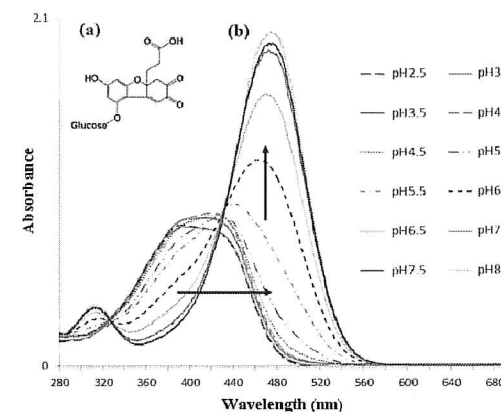
**Figure 2.** Cyclic voltammograms of 1.8 mM POP<sub>j</sub> in 0.1 M Phosphate buffer solutions, recorded at pH 3, 5 and 8. Glassy carbon disk electrode (2 mm), Pt counter electrode, Ag/AgCl reference electrode.

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**Figure 1.** (a) Structure of the POP<sub>j</sub>. (b) Evolution of the UV-visible spectrum of POP<sub>j</sub> according to pH.

Moreover, during the fermentative process in cider making industry, changes occur in the redox potential of the musts and a discoloration of the products is clearly observed. We proposed that the exposure of some colored polyphenols to those reducing conditions could result in a switch to their reduced colorless form. In order to validate this hypothesis, we carried out model studies on both cider model chromophores by electrochemical methods. It was explored by cyclic voltammetry and UV-visible spectroelectrochemistry. The POP<sub>j</sub> is easier to reduce when the pH value decreases (Fig. 2). In real time measurement, we clearly observed a hypsochromic shift on UV-visible spectrum when the molecule is reduced at the electrode. It was confirmed by conducting a bulk electrolysis at pH 3.7 leading to a clear discoloration. The resulting solution was analyzed by HPLC-DAD-MS. As we expected, the reduction led to a conversion of POP<sub>j</sub> into its reduced colorless form POP<sub>i</sub> but other colorless and still unknown compounds were also produced at the electrode.