Synthesis and Characterization of New Flavylium Compounds With a Phenyl Group

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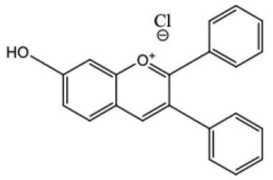

Abstract

Anthocyanins are glycosylated derived red-purple-blue flavonoid pigments found in the outer layer of plant structures such as fruits, vegetables, flowers. The core structure of anthocyanins is the flavylium cation. Anthocyanidins are plan pigments formed by the hydrolysis of anthocyanins, characterized by the same flavonoid structure without glucose on the number 3 carbon of the C ring of the flavylium cation. Those colored pigments can be used as a dye in Dye-Sensitized Solar Cells (DSSC) and as a sensor or therapeutic compound for diseases caused by protein aggregation. Flavylium compounds with a phenyl group, 7, 8-dihydroxy-4'-phenyl flavylium, 7,8- dihydroxy-3-phenyl flavylium, and 7-hydroxy-3 phenyl flavylium were synthesized using Aldol condensation. The products were confirmed and characterized by UV/Vis, IR, and NMR spectroscopies. In this presentation, the synthesis and characterization of the flavylium compounds will be discussed.

Anthocyanin's

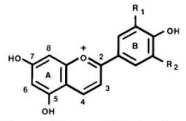

Figure 1: Structure of Flavylium Ion

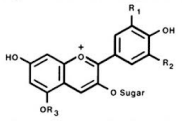

Figure 2: Structure of Anthocyanin

Anthocyanin's are red, purple, and blue water-soluble pigments found in the outer layer of plant structures such as fruits, vegetables, plants. Berries, currants, grapes, red to purplish blue-colored leafy vegetables, grains, roots contain a high levels of anthocyanin. Aside from fruits and vegetables they are found in edible flowers. Some of which have been traditionally used as folk medicine, colorants and as food. The basic core structure is the 2-phenyl-benzopyrylium (Flavylium) ion.

Reaction Scheme of Synthetic Anthocyanidins

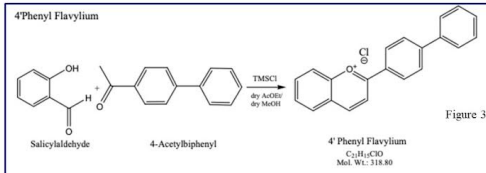

Figure 3: Scheme of 4'Phenyl Flavylium

Equimolar amounts (1mmol) of Salicylaldehyde and 4-Acetylbiphenyl were dissolved in 5 mL of AcOEt/MeOH (4/1, v/v). After cooling to 0 °C, 10mmol TMSCl was added. The mixture was stirred for 10 min, then kept at 4 °C for 3 days. Precipitation of pigment was achieved by adding AcOEt. The product was obtained by filtration.

Reaction Mechanism of 4'Phenyl Flavylium ion

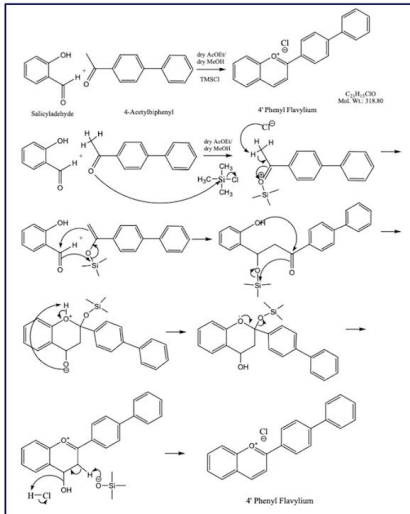

Figure 4:Aldol Mechanism of 4'-Phenyl Flavylium

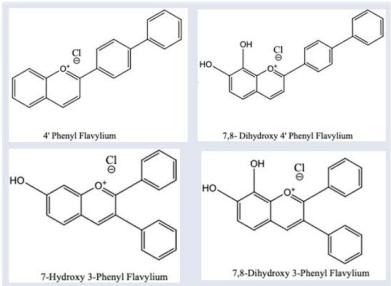

Figure 5: Structures of Synthesized Anthocyanidins

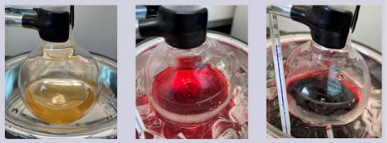

Figure 6: Color Change of 7-Hydroxy 3-Phenyl Flavylium Throughout The Synthesis.

Uv-Vis Spectra of Synthetic Anthocyanidins

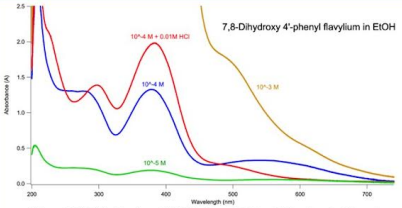

Figure 7: UV-Vis Spectra of 7,8-Dihydroxy 4'-Phenyl Flavylium in Ethanol

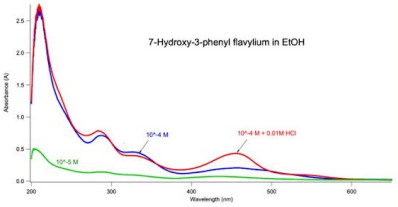

Figure 8: UV-Vis Spectra of 7-Hydroxy 3-Phenyl Flavylium in Ethanol

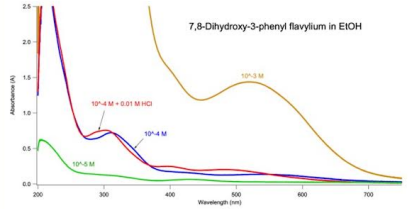

Figure 9: UV-Vis Spectra of 7,8-Dihydroxy 3-Phenyl Flavylium in Ethanol

Results and Discussion

	4'-Phenyl Flavylium	7,8-Dihydroxy 4'-Phenyl Flavylium	7-Hydroxy 3-Phenyl Flavylium	7,8-Dihydroxy 3-Phenyl Flavylium
% Yield	3.9%	87.7%	45.8%	11.68%

Table 1: % Yield of Artificially Synthesized Anthocyanidins

- Each pigment was dissolved in ethanol, at different concentrations: 10^{-3}M, 10^{-4}M, 10^{-5}M. Most ideal concentration was determined to be 10^{-4}M, neither too concentrated for measurements nor too diluted.
- The compounds exist in 4 isomers, which have absorbances at different wavelength ranges.
- 7,8-Dihydroxy 4'-Phenyl Flavylium, in 10^{-4}M solution shows an increased absorption ~580nm, in comparison to acidic conditions in figure 7. There is more intense light absorption in acidic conditions as depicted at ~380nm. The compound has red-shifted in acidic conditions.
- 7-Hydroxy 3-Phenyl Flavylium, in 10^{-4}M solution shows a reduced absorption ~450nm, in comparison to acidic conditions in figure 8, which might be due to π stacking. There are two absorption peaks ~270nm and ~340nm. The compound has blue-shifted in acidic conditions.
- 7,8-Dihydroxy 3-Phenyl Flavylium, in 10^{-4}M solution has one primary absorption peak~310nm, which is increased in acidic conditions in figure 9.
- 7-Hydroxy 3-Phenyl Flavylium and 7,8-Dihydroxy 3-Phenyl Flavylium have phenyl groups in the carbon 3 position, due to static hindrance, the conjugation gets distorted, absorbing less light. Hence both Figures 8 and 9 show low absorbances.
- All three compounds have 4 benzene rings, as seen in all three figures 7, 8, and 9 the compounds have high absorption peaks ~230nm.

Selected References

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