Asian Journal of Research in Botany

4(2): 11-15, 2020; Article no.AJRIB.58129

Semi-synthetic Color Reaction Chemistry of Furan Ring Anellated Flavonoids

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Authors' contributions

This work was carried out in collaboration between both authors. Author MSAA designed the project and performed all experiments. Author MAT supported in data management, manuscript writing and submission. Author MSAA wrote the first draft of manuscript. Both authors read and approved the final manuscript.

Article Information

Editor(s):
(1) Dr. Ogbonna, Abigail Ifemelunma, University of Jos, Nigeria.
Reviewers:
(1) Kendeson A. Christiana, Federal University of Kashere, Nigeria.
(2) B. Hari Babu, Acharya Nagarjuna University, India.
(3) Jorge A. López, Tiradentes University, Brazil.
Complete Peer review History: http://www.sdiarticle4.com/review-history/58129

Original Research Article

Received 10 April 2020
Accepted 16 June 2020
Published 23 June 2020

ABSTRACT

Color reaction chemistry of furan ring anellated flavonoids was explored. Structurally different furanoflavonoids gave reaction products with different color hues. Efforts were made to establish structure-color reaction chemistry of products mechanistically and theoretically.

Keywords: Furanoflavonoids; secondary metabolites; color reactions; semi-synthesis.

1. INTRODUCTION

Furo-anellated flavonoids or furanoflavonoids belong to special secondary metabolite class of flavonoids found in selected plants varieties around the globe [1]. Furan ring fused with aromatic segment of 1-benzopyran-4-one (chromone) nucleus is the characteristic structural feature that distinguishes furanoflavonoids from other members of substituted flavonoids family [2,3].

It is a known scientific fact that flavonoids derivatives are the source of color in different

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part of plants like flowers and fruits. In many instances the color of skin of fruits or petals of flowers is the cumulative color emission response of conjugated compounds present in them [4,5]. Furanoflavonoids were discovered from species of family leguminosae. The fused heterocyclic structural feature attached to benzopyran nucleus of flavonoids offer an extended conjugation characteristic to a molecule as a whole when change to flavylium salt [6].

The current study is based on Shinoda test performed in lab to study structural modification (semi-synthesis) of purified furo-anellated flavonoids isolated from *Pongamia pinnata* (Linn.) specie located in North Eastern Region of Punjab, Pakistan.

Literature survey revealed that the most distinguishable and productive color test in identification of furo-flavonoids was found to be Shinoda reaction [7]. This test is based on the reduction reaction of flavonoids in the presence of Mg-HCl. Shinoda chemical test convert flavonoids into their flavylium salt.

2. MATERIALS AND METHODS

Extraction and purification of targeted secondary metabolites from seed oil of *Pongamia pinnata* (Linn.) have been reported earlier [8]. The photographs of the developed chromatograms of all the isolated compounds (1= Pongapin, 2 = Karanjin, 3 = Kanjone, 4 = Lanceolatin-B as standards and 5 = Sample mixture) were taken under the UV light taken at 256 nm (Fig. 1). Since these digital photographs closely reflect the original chromatograms, therefore they may serve as visual reference of these compounds for future research work. Solvents used for this study were ethanol (Merck) and anhydrous aluminum chloride salt (RDH).

The snap shots of colored reaction mixtures as conclusive evidence were recorded using in built camera of Nokia (6230) cell phone. Shinoda test was performed on all isolated compounds by employing a slightly modified method reported earlier [9]. Solutions of compounds were prepared in ethanol, few magnesium turnings were added to the solutions followed by drop wise addition of conc. HCl. The appearance of any color in sample solutions were noted and recorded photographically.

2.1 Mechanism

In general, the possible mechanism of flavone to flavylium salt may be consists of following steps.

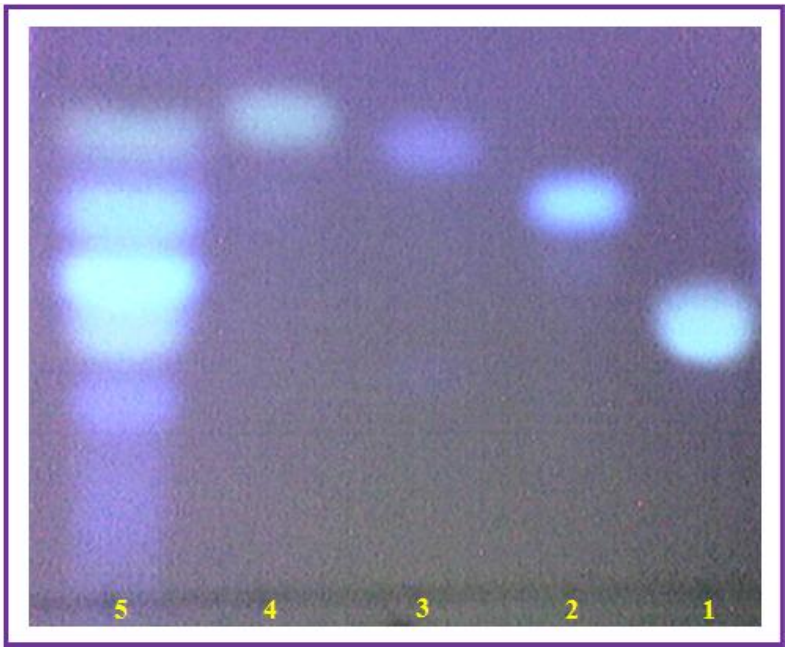


Fig. 1. Developed chromatogram of isolated compounds

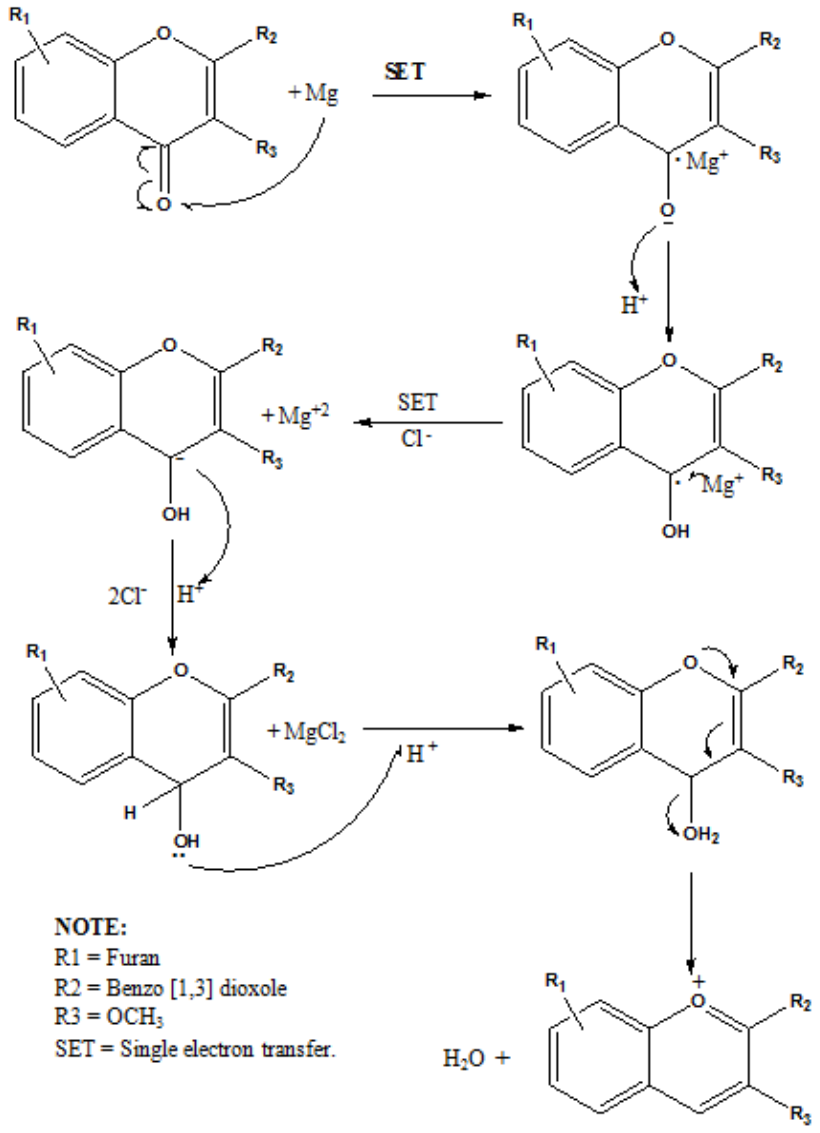
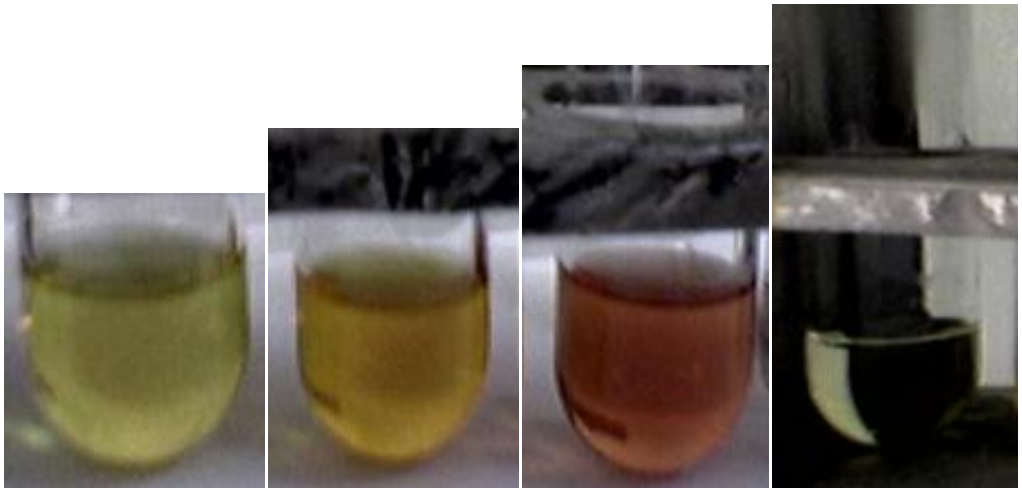


Fig. 2. Reduction mechanism of pongapin into its flavylium salt

1. Mg metal plays as catalyst and provides 1st electron to Oxygen.
2. One electron moves to carbon and other shifted to Oxygen as a result of homo splitting of double bond. So Oxygen attain a lone pair (one from Mg and other from double bond) and by using it, makes coordinate covalent bond with proton of acid.it may be noted that attachment of proton with oxygen of ether linkage is not favorable due to stability.
3. Carbonyl carbon attain negative charge (one electron from breakage of double bond and other from Mg metal) and makes coordinate covalent bond with proton of acid.
4. Mg^{+2} combines with two Cl^{-1} (from acid) to form $MgCl_2$.
5. Loan pair at OH attacks proton of acid to make water which is good leaving group. Oxygen of ether linkage attain positive charge by shifting loan pair towards right. Vertical double bond moves next to facilitate removing of water molecule.
6. This process generates extended conjugation over the entire molecule (flavylium salt) which cause color of compound.



a b c d

Fig. 3. Shinoda test for a (pongapin), b (karanjin), c (kanjone) and d (lanceolatin-B)

The flavylium cation owing to its extensive conjugation system readily absorbs in the visible region of spectrum, thus impart color to the solution. Schematic mechanism of reduction process of Pongapin is shown in Fig. 2.

3. RESULTS AND DISCUSSION

In our study, total four furanoflavonoids were isolated, purified and characterized spectroscopically, namely Pongapin, Karanjin, Kanjone, and Lanceolatin-B. When treated with Mg-HCl, the reaction mixture of furanoflavonoid of Pongapin gave light yellow (570 nm) color (a). Shinoda test of furanoflavonoid for Karanjin was positive and changes its color in a reaction mixture from colorless to bright yellow (590 nm) (b). In case of Kanjone, the colorless reaction mixture turned brown (600 nm) (c) whereas reaction mixture of furanoflavonoid Lanceolatin-B gave very light yellow (580 nm) colored hue (d). Shinoda color test for all the four furanoflavonoids is shown in Fig. 3.

4. CONCLUSION

Color reaction chemistry of few furan ring anellated flavonoids isolated and purified from seed oil of *Pongamia pinnata* (Linn.) was explored by employing a valuable productive Shinoda reduction test. Colored reaction shows that reactants are converted into colored flavylium salt of furanoflavonoids.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle4.com/review-history/58129