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Visible Light Induced Knoevenagel Condensation Catalyzed by Starfruit Juice of *Averrhoa carambola*

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Abstract

Aqueous starfruit juice catalyzed a simple and efficient Knoevenagel condensation of aromatic aldehydes with malononitrile has been developed under visible light. Products were obtained in yields up to 98% after short reaction times and they were isolated by simple filtration in pure crystallization states. The method is green and economically viable. A plausible mechanism for photochemical Knoevenagel condensation reaction catalyzed by starfruit juice was also predicted.

Keywords

Knoevenagel Condensation, Aqueous Starfruit Juice, Aldehydes, Malononitrile, Visible Light

1. Introduction

Knoevenagel condensation, first demonstrated by Emil Knoevenagel in 1894 [1], is one of the most important and widely employed methods for carbon-carbon double bond formation in synthetic chemistry [2]-[4]. It has been used for the preparation of a wide range of substituted electrophilic alkenes, and for the synthesis of intermediate such as coumarin derivatives which are useful in perfumes, cosmetics and bioactive compounds [5]-[8]. In addition, Knoevenagel condensation products exhibit inhibition of antiphosphorylation of EGF-receptor and antiproliferative activity [9]. As a result of their importance from a pharmacological, industrial and synthetic point of view a large number of methods for the Knoevenagel condensation have been reported using various Lewis bases/acids [10]-[14]. The use of Green Chemistry protocol based on microwave assisted reaction [15]-[20], ultrasound irradiation [21] [22], biotechnology-based approach [23] [24], solid phase [25] [26], green solvent like ionic liquid [27]-[33] or water [34]-[36], and grindstone method under solvent-free condition [37]-[39]

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have also been developed. It is noteworthy to observe that all these protocols have some drawbacks, such as use of expensive catalyst, high thermal conditions, disposal of toxic solvents and catalyst, long reaction time often pose a problem.

In the past two decades, classical organic chemistry had been rewritten around new approaches that search for products and processes in the chemical industry that are environmentally acceptable [40]. Therefore, to address depletion of natural resources and preservation of ecosystem is just urgent to develop so called "greener technologies" to make chemical agents for well being of human health [41].

An attractive area in organic synthesis involves photochemical reactions particularly using visible light in environment-friendly solvent like water or aqueous ethanol and is generally considered as a clean and green procedure. This type of photo-activation of substrate very often minimizing the formation of by-products and for this reason, photochemical reactions occupy an interesting position and excellent reviews/paper have been published [42]-[47]. The use of water as a reaction medium is not only inexpensive and environmentally benign but also provides completely different reactivity [48]. It has been suggested that the effect of water on organic reaction may be due to the high internal pressure exerted by a water solution which results from the high cohesive energy of water [49].

A number of organic reactions using natural catalysts such as clay [50]-[53], natural phosphate [54] [56], animal bone [57], and also various fruit juice's are reported in literature. Due to acidic nature, aqueous fruit juice like lemon [58]-[64], pineapple [65] [66], coconut [67], *Acacia concinna* [68], *Sapindus trifolistus* [69] and *Tamarindus indica* [70] [71] fruit has been found to be a suitable replacement for various homogeneous acid catalysis. In accordance with this, we report the Knoevenagel condensation of aromatic aldehydes with malononitrile in presence of aqueous starfruit juice, a natural, green and biocatalyst system stimulated by visible light.

Starfruit (*Averrhoa carambola*) (**Figure 1**) is grown extensively in Philippines, Indonesia, Malaysia, India, Bangladesh, Latin America and Sri Lanka. It has long been one of the most popular of the citrus tropical and subtropical fruits, largely because of its attractive flavor and refreshing sugar-acid balance. Starfruit juice of *Averrhoa carambola* shows antioxidant properties due to scavenging of nitric oxide (NO) and antimicrobial activities against *E. coli*, *Klebsiella spp*. and *Staphylococcus aureus* [72].

The main ingredients [73] [74] of 100 gm of unripe starfruit contain water (89 - 91 g), protein (0.38 g), fat (0.08 g), carbohydrates (9.38 g), sugars (3.98 g), edible fiber (0.8 - 0.9 g), calcium (4.4 - 6.0 mg), phosphorous (15.5 - 21 mg), sodium (2 mg) and potassium (133 mg). Fresh mature unripe fruit were found to have a total acid content of 12.51 mg consisting of 5 mg oxalic acid, 4.37 mg tartaric acid, 1.32 mg citric acid, 1.21 mg malic acid, 0.22 mg succinic acid, 0.26 - 0.53 mg ascorbic acid and 0.39 mg pantothenic acid. The composition of the starfruit juice varies with geographical, cultural and seasonal harvesting and processing. An aqueous extract of starfruit juice is acidic due to presence of edible organic acids and hence it will be work as an acid catalyst for acid catalyzed reactions.

2. Results and Discussion

In continuation of our research interest concerning the investigation of new natural catalyst and development of

Figure 1. Photoghrapy of starfruit of *Averrhoa carambola.*

new methodologies (62 - 64, 70, 71) herein is reported in this paper, for the first time a highly efficient, eco-friendly and economic method for Knoevenagel condensation of aldehydes with malononitrile using aqueous starfruit juice stimulated by visible light affording 2-(substituted phenylidene) malononitrile (**Scheme 1**).

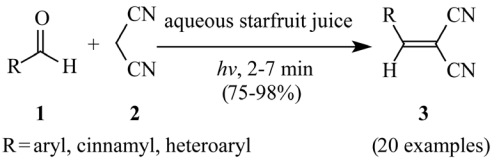
The photochemical reactions were found to be very clean and the products were obtained in extremely pure crystalline states with an average yield of 75% - 98% and the reaction time varied on an average 2 - 7 min. The products were isolated from the reaction mixture in pure crystalline form by cooling in an ice-bath and need no further crystallization for aromatic aldehydes and the results are given in **Table 1**.

The scope of application of the presented method is demonstrated by using various substituted aromatic aldehydes to react with malononitrile. The procedure was successfully applied for heteroaromatic aldehydes (entries 18, 19), and the ether (entries 3, 9, 15, 16), esters (entries 14, 15) linkages in the aromatic aldehydes were unaffected under photochemical conditions. The reaction was further explored for the synthesis of *p*-bis-2-(phenylidene) malononitrile (**3t**) in 95% yield by the condensation of terephthalaldehyde (entry 20) with two mole of malononitrile under similar reaction conditions.

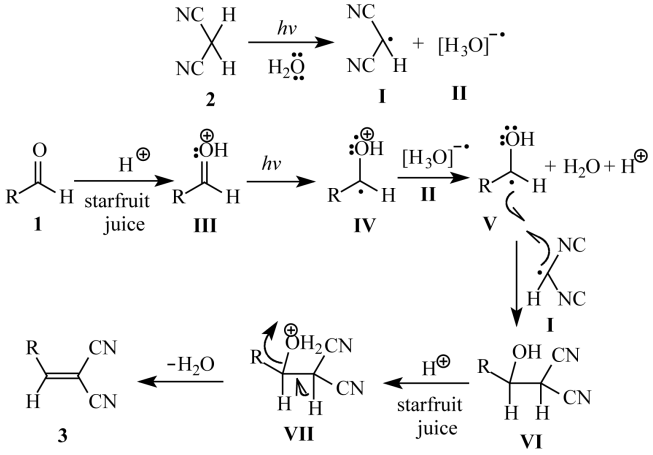
When the same reactions were performed at room temperature for 1 h, only 30% - 35% of the corresponding products were isolated. On the hand, under refluxing conditions for 10 min only 30% - 40% of **3** were isolated and the yield of the products increased to 60% - 65% after 3 - 4 h. The microwave irradiation reaction, accomplished in an average time periods 2 - 3 min. In all the above cases products were isolated by column chromatography or required further crystallization from appropriate solvents. Thus, the present method in comparison with room temperature, thermal and microwave irradiation one, is encouragingly effectual and smoothly for aromatic aldehydes free from any adhering by byproduct or side products.

In the present instance, we speculate that the reaction may plausibly be initiated by homolytic C-H bond cleavage of malononitrile (**2**) in the presence of light to produce a radical **I** and hydrogen radical which is immediately converted to a transient anion radical **II** due to a weak interaction with water molecules. Aldehyde (**1**) becomes activated by protonation from starfruit juice to produce a protonated species **III**. One electron transfer from **II** to **IV** produced a radical **V**, which couples with radical **I** to form **VI**. Protonation of **VI** followed by dehydration from **VII** to form the title compound **3** as depicted in **Scheme 2**.

All the products (**Table 1**) are known compounds and their structures are confirmed by comparison of melting

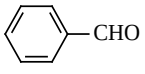
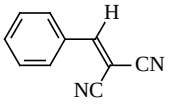
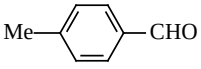
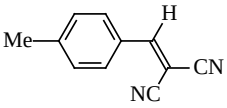
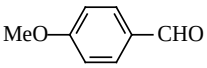
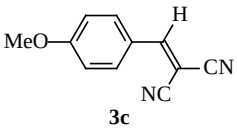
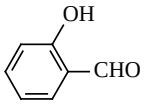
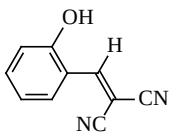
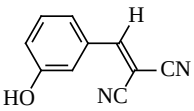
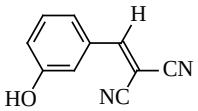
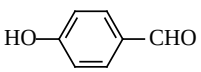
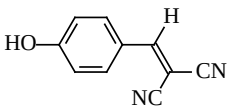
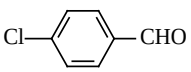
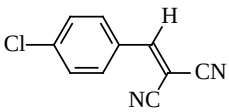
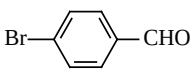
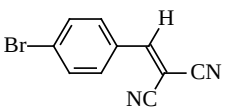
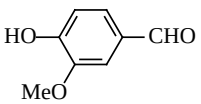
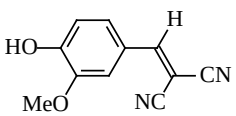
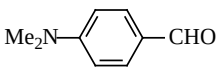
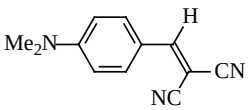


Scheme 1. Visible light induced Knoevenagel condensation reaction catalyzed by starfruit juice.



Scheme 2. Plausible mechanistic pathway for the photochemical Knoevenagel condensation of aldehydes and malononitrile catalyzed by starfruit juice.

Table 1. Results of photochemical Knoevenagel condensation of aldehydes with malononitrile catalyzed by aqueous star-fruit juice.

Entry	Substrate (1)	Product (3)[a]	Yield (%)[b]	Time (min)	M.p.(˚C) [Lit. Value][c]
1	 **1a**	 **3a**	92	3	81 - 82 [80]-[83][37]
2	 **1b**	 **3b**	94	4	133 - 134 [134] [135][27]
3	 **1c**	 **3c**	85	5	113 - 115 [116][66]
4	 **1d**	 **3d**	75	4	160 [159][66]
5	 **1e**	 **3e**	95	2	165 [164][71]
6	 **1f**	 **3f**	82	4	182 - 184 [185] [186][20]
7	 **1g**	 **3g**	93	4	164 - 166 [162]-[164][19]
8	 **1h**	 **3h**	80	7	158 [156][66]
9	 **1i**	 **3i**	92	6	132 - 134 [135] [136][20]
10	 **1j**	 **3j**	90	5	182 [180][22b]

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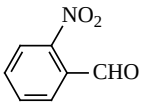
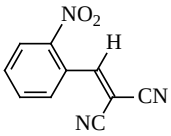
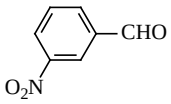
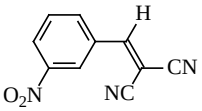
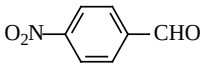
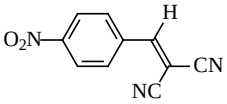
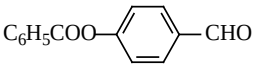
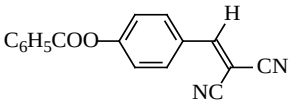
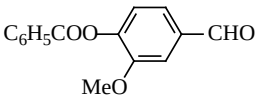
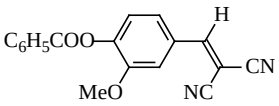
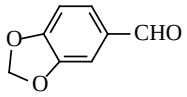
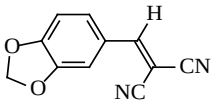
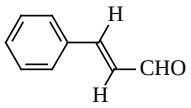
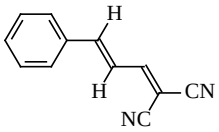
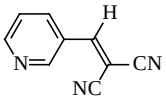
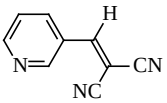
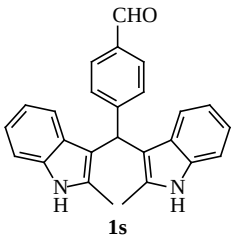
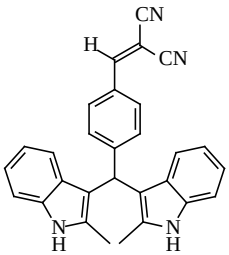
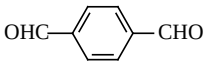
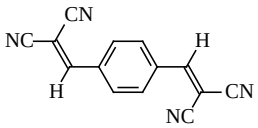
11	 **1k**	 **3k**	95	3	134 [136]-[138][27]
12	 **1l**	 **3l**	88	4	104 - 106 [107] [108][20]
13	 **1m**	 **3m**	90	2	161 - 163 [160]-[162][19]
14	 **1n**	 **3n**	94	7	152 - 154 [152][71]
15	 **1o**	 **3o**	92	7	140 - 141 [140] [141][71]
16	 **1p**	 **3p**	98	4	200 - 202 [198][71]
17	 **1q**	 **3q**	78	5	125 - 127 [127]-[129][37]
18	 **3r**	 **3r**	90	3	80 - 82 [84] [85][27]
19	 **1s**	 **3s**	78	7	320 - 322 [320]-[322][71]
20	 **1t**	 **3t**	95	3	300 [298]-[300][71]

[a]All products were identified by their physical and spectral data; [b]Isolated yields; [c]References for literature melting point.

points and spectral data with their literature data.

3. Conclusion

We have described a potentially efficient, absolutely clean, and high yielding eco-friendly methodology, for the photochemical Knoevenagel condensation of various aromatic aldehydes with malononitrile catalyzed by aqueous starfruit juice. The present protocol devoid of any toxic catalysts, solvents or solid supports and may be considered as an excellent improvement over the existing methods.

4. Experimental Section

All reactions were run in dried glassware. Reagents were purchased (Spectrochem or SRL or LOBA) and used without further purification. Melting points were determined on a Kofler block and uncorrected. Reactions were irradiated in a 200 W tungsten lamp (Philips India Ltd). ^{1}H and ^{13}C NMR and spectra were obtained in $CDCl_3$ or DMSO-d_6 on a Bruker AV-300 (300 MHz) spectrometers using TMS as an internal standard. Analytical samples were dried *in vacuo* at room temperature. The carbon, hydrogen and nitrogen percentages in synthesized products were analyzed by Perkin-Elmer 2400 series II C, H, N analyzers. Thin layer chromatography was carried out on silica gel.

4.1. Preparation of Aqueous Extract of Starfruit Juice

The mature green starfruit were purchased from the local market. The starfruit were cut into pieces with the help of knife. The hard green material (20 g) was boiled with water (50 ml), cooled and it was centrifuged using micro centrifuge (REMI RM-12C). The clear portion of the aqueous extract (pH = 3.5) of the starfruit was used as catalyst for the reactions.

4.2. General Procedure for Photochemical Knoevenagel Condensation Reaction

Different aromatic aldehydes (**1a-s**) (10 mmol) or (**1t**) (5 mmol), malononitrile (10 mmol), and aqueous starfruit juice (5 ml, pH = 3.5) were taken in a round bottomed flask and irradiated with a 200 W tungsten lamp (Philips India Ltd). The reaction time varied from 2 - 7 min monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled and the crystalline products (**3a-t**) so obtained was filtered, washed with water and dried in vacuo. The Knoevenagel condensation products were isolated in excellent yields in essentially pure form.

4.3. Spectral Data for Some Selected Compounds

2-(3-*Hydroxyphenylmethylene*)*malononitrile* (**3*e***): Yellow crystal, Yield: 95%, mp. 165˚C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.08 (d, 7.5 Hz, 1H), 7.35 - 7.44 (m, 3H), 8.44 (s, 1H, H-C=C), 10.12 (s, 1H, OH); Anal. Calcd. for $C_{10}H_6N_2O$, C, 70.58; H, 3.55; N, 16.46%, found C, 70.22; H, 3.87; N, 16.21%.

2-(4-*Benzoyloxyphenylmethylene*)*malononitrile* (**3*n***): Colorless crystal, Yield: 94%, mp. 152˚C - 154˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (d, 8.7 Hz, 2H), 7.54 (t, 7.5 Hz, 2H), 7.66 - 7.78 (m, 1H), 7.78 (s, 1H, H-C=C), 8.01 (d, 8.7 Hz, 2H), 8.20 (d, 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 82.54 (=C<), 112.49 (CN), 113.61 (CN), 123.12, 128.41, 128.53, 128.75, 130.29 (-CH=), 132.37, 134.20, 155.56, 158.56, 164.24 (ester carbonyl); DEPT - 90 (75 MHz, $CDCl_3$): 123.11, 128.74, 130.28, 132.35, 134.18, 158.52; DEPT - 135 (75 MHz, $CDCl_3$): 123.11, 128.74, 130.28, 132.35, 134.18, 158.51; Anal. Calcd. for $C_{17}H_{10}N_2O_2$, C, 74.45; H, 3.67; N, 10.21%, found C, 74.11; H, 3.81; N, 10.43%.

2-(4-*Benzoyloxy*-3-*methoxyphenylmethylene*)*malono-nitrile* (**3*o***): Colorless crystal, Yield: 92%, mp. 140˚C - 141˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H, OMe), 7.34 (d, 8.4 Hz, 1H), 7.43 (dd, 8.7 and 1.8 Hz, 1H), 7.53 (t, 7.5 Hz, 2H), 7.64 - 7.69 (m, 1H), 7.74 (d, 1.8 Hz, 1H), 7.76 (s, 1H, H-C=C), 8.20 (d, 8.7 Hz, 2H);

Anal. Calcd. for $C_{18}H_{12}N_2O_3$, C, 71.05; H, 3.97; N, 9.21%, found C, 70.85; H, 4.02; N, 9.52%.

2-(3,4-*Methylenedioxyphenylmethylene*)*malononitrile* (**3*p***): Yellow crystal, Yield: 98%, mp. 200˚C - 202˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.12 (s, 2H, -O-CH_2-O-), 6.93 (d, 8.1 Hz, 1H), 7.32 (dd, 8.1 and 1.5 Hz, 1H), 7.59 (s, 1H, H-C=C), 7.60 (s, 1H); Anal. Calcd. for $C_{11}H_6N_2O_2$, C, 66.67; H, 3.05; N, 14.14%, found C, 67.01; H, 3.21; N, 14.32%.

2-[{*p*-3, 3'-*Bis*(2-*methylindolyl*)*methyl*}*phenyl-methylene*]*malononitrile* (**3*s***): Pale-yellow crystal, Yield: 78%, mp. 320˚C - 322˚C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 6H, Me), 6.04 (s, 1H, Ar-CH), 6.84 - 6.93 (m, 4H), 7.06 (t, 6.9 Hz, 2H), 7.28 (d, 9.0 Hz, 2H), 7.44 (d, 8.1 Hz, 2H), 7.72 (s, 1H, H-C=C), 7.80 (d, 8.7 Hz, 2H), 7.80 (br. s, 2H, NH); Anal. Calcd. for $C_{29}H_{22}N_4$, C, 81.67; H, 5.20; N, 13.14%, found C, 81.33; H, 5.40; N, 13.25%.

p-Bis-2-(*phenylmethylene*)*malononitrile* (**3*t***): White crystal, Yield: 95%, mp. 300˚C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.09 (s, 4H), 8.63 (s, 2H, H-C=C); ^{13}C NMR (75 MHz, DMSO-d_6): δ 84.71 (=C<), 112.14 (CN), 113.80 (CN), 130.83 (-CH=), 135.32 (aromatic quarternary), 159.80 (aromatic -CH=); DEPT - 90 (75 MHz, DMSO-d_6): 130.83, 159.81; DEPT - 135 (75 MHz, DMSO-d_6): 130.84, 159.81; Anal. Calcd. for $C_{14}H_6N_4$, C, 73.04; H, 2.63; N, 24.34%, found C, 72.95, H, 2.76; N, 24.45%.

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