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Biocatalyst mediated synthesis of tryptanthrins performed under ultrasonication

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The concomitant exploitation of two of the green chemistry tools *viz*., sonication and biocatalysis is reported here for the synthesis of natural alkaloid, tryptanthrin (indolo[2,1-*b*]quinazoline-6,12-dione). High intensity ultrasound has been applied to facilitate the release of enzymes by disruption of cells of baker's yeast (*Saccharomyces cerevisae*) as a biocatalyst. The coupled system is an excellent instance of enhanced rate of biocatalyzed reaction and has proven to be a green alternative to existing methodologies for the synthesis of tryptanthrins. The present method is bestowed with merits such as mild and clean reaction conditions, operational simplicity, tolerance for a wide variety of substituents, green aspects through the avoidance of toxic metal catalysts and highly selective conversion with no byproducts.

Keywords: Ultrasonication, tryptanthrin, alkaloids, biosynthesis, baker's yeast

The fundamental challenge for today's researchers is the development of synthetic methodologies with environmental and economic benefits. In this scenario biocatalysis is one of the green methods in organic synthesis due to mild reaction conditions and remarkable chemo, regio and stereoselectivities with no side products[1]. Biocatalysis refers to the use of enzymes or enzyme containing cells in chemical transformations. Biocatalysts are nature's sustainable catalysts, derived from renewable sources and are biocompatible, biodegradable, essentially non-toxic and non-hazardous. Naturally, biocatalysts work efficiently in aqueous environment but it is not of much use for most of the organic reactions as substrates are insoluble in aqueous medium. Therefore, the use of biocatalyst in organic solvent is gaining much importance. The advantages of biocatalyst in organic solvent are high solubility of organic substrates, ease of product isolation and insolubility of biocatalyst in organic solvents which permits their easy recovery and reuse[2]. Literature survey reveals that, biocatalysts have pathbreaking catalytic activity in non-natural reactions[3–5]. Among the various biocatalysts used in organic transformations, baker's yeast (*Saccharomyces cerevisiae*) has emerged as one of the frequently employed microorganisms in whole cell form due to low cost, easy availability and safe handling. Baker's yeast is found to display its catalytic potential in non-aqueous medium[6,7]. Recently, Mane and coworkers have studied the catalytic activity of baker's yeast in non-aqueous medium for the synthesis of biodynamic heterocycles[8,9]. In addition, baker's yeast has been used under ultrasonication for the synthesis of isoindolo[2,1-*a*]quinazolines[10] and 1,4-benzothiazines[11]. Ultrasonication has been explored as an innovative and more effective tool for the disruption of cells of baker's yeast to release enzymes[12,13]. Disruption of yeast cell is generally easier because of their larger size and different cell wall structure. The basic structural component of yeast cell wall have been well identified as proteins which are enzymes rather than structural components[14].

Tryptanthrin is a natural product characterized by a novel indolo[2,1-*b*]quinazoline ring system. Tryptanthrin and several related alkaloids, such as candidine, phaitanthrins A–E, methylisatoid and cruciferane (Figure 1) have been found in number of plant species[15] and show broad spectrum of biological activities. The biological activity demonstrated by tryptanthrin and its derivatives pertains to antitumor, antiprotozoal, antiparasitic, antineoplastic, antileishmanial and antitubercular properties[16,17]. It shows excellent cytotoxicity against human breast carcinoma (MCF–7), lung carcinoma (NCI–H460) and central nervous system carcinoma (SF–298) cell lines[18]. In addition, the inhibitory activity of tryptanthrin against cyclooxygenase (COX–2), 5-lipoxygenase (LOX), nitric oxide synthase (NOS), indoleamine 2,3-dioxygenase and prostaglandin E(2) expression has been reported[19].

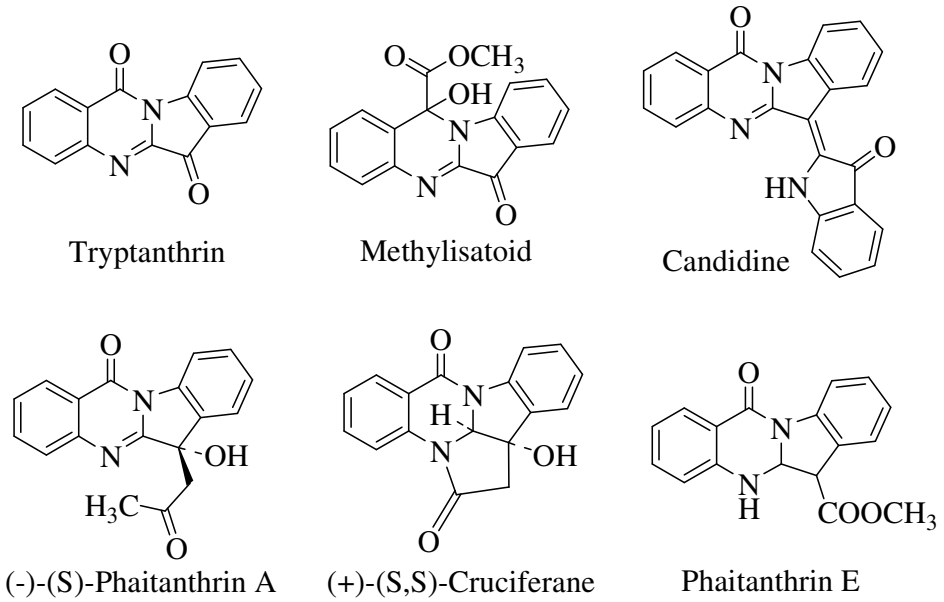


Figure 1 — Tryptanthrin and related alkaloids

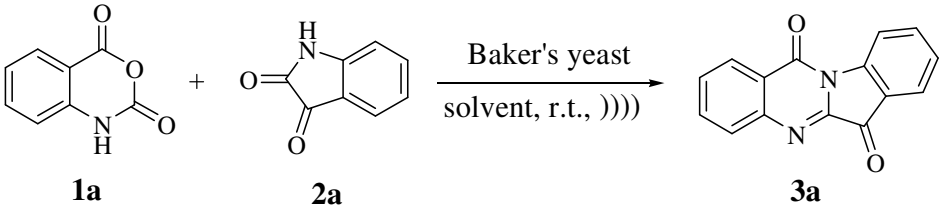
Tryptanthrin has attracted much attention as an aryl hydrocarbon receptor agonist[20], inducer of caspase-3/ Fas mediated apoptosis[21] and as anti-inflammatory agent[22]. Furthermore, the physicochemical properties of tryptanthrin compounds and usefulness of tryptanthrin derivatives as dyes, pigments and photoelectric materials have also been investigated[23,24].

In view of the promising bioactivities of tryptanthrin and its synthetic congeners, they have been imperative targets of numerous synthetic studies. The most common synthetic approach to indolo[2,1-*b*]quinazoline core depends on the use of isatin through the reaction of isatin with isatoic anhydride[25], treatment of isatin with $POCl_3$[26], cathodic reduction of isatin[27], coupling of *ortho*-aminobenzoic acid with isatin using $SOCl_2$[28] and tert-butyl hydroperoxide/ K_3PO_4 promoted oxidative cyclization of isatins[29]. Moreover, the reaction of 2-bromophenyl isocyanide with electrophilic methyl-2-isocyanatobenzoate[30], I_2-tert-butyl hydroperoxide catalyzed intramolecular amination[31], insertion of aryne intermediate to quinazolinones[32] and copper catalyzed reaction[33] have been developed for the synthesis of tryptanthrin. Oxidative dimerization of isatin or indole including oxidation of isatin with $KMnO_4$[34], copper catalyzed oxidation of indole[35], Dakin oxidation of indole-3-carbaldehyde[36] and oxone induced oxidation of indole-3-carbaldehyde[37] also led to the formation of tryptanthrin. Very recently Cobalt(III)–porphyrin complex (CoTCPP) has been used as a catalyst for the synthesis of tryptanthrin in aqueous media[38]. Unfortunately, these reported transformations of reactant materials into target molecules involve a number of chemical operations/steps in which harsh reaction conditions, expensive and toxic catalysts, *etc.* are used. As a result, along with desired products, waste material is generated which is environmentally unsafe. In terms of green chemistry, the produced waste should be regenerated, destroyed or disposed off, instead it consumes much energy and disturbs the ecosystem. Therefore, it is very much essential to modify the conventional reaction conditions and develop environmentally useful methodologies in which less byproducts/waste is produced. In this context, the exploration of an efficient, easily available catalyst with high catalytic activity for the synthesis of tryptanthrins is strongly desirable.

Considering the above facts and in continuation of our interest in biocatalyzed reactions[39–43] and sonocatalysed organic transformations[44] herein, we disclose a novel methodology for the synthesis of tryptanthrin derivatives from condensation of isatoic anhydrides and isatins in organic solvent using baker's yeast as catalyst under ultrasonication.

Results and Discussion

In order to obtain the best experimental conditions, we have considered reaction of isatoic anhydride **1a** with isatin **2a** in the presence of baker's yeast as standard model reaction to get the product **3a** (Scheme I).



1a **2a** **3a**

Scheme I — Synthesis of indolo[2,1-*b*]quinazoline-6,12-dione using baker's yeast under ultrasound irradiation

Table I — Effect of solvent on the reaction of isatoic anhydride and isatin catalyzed by baker's yeast [a]

Entry	Solvent	Without Ultrasound [b]		With Ultrasound [c]	
		Time (h)	Yield [e] (%)	Time (h)	Yield [e] (%)
1	Water	24	n.d.	4	n.d.
2	Ethanol	24	30	4	35
3	Methanol	24	34	4	40
4	Dichloromethane	24	40	4	48
5	Dimethyl Formamide	24	30	4	45
6	Acetonitrile	24	24	4	62
7	Tetrahydrofuran	24	52	3	88
8	Tetrahydrofuran	24	54	3	86 [d]

[a] Reaction conditions: isatoic anhydride (1 mmol), isatin (1 mmol), baker's yeast (400 mg) and solvent 5 mL. Reaction temperature 30°C.
[b] Reaction without ultrasound. Reaction temperature 30°C.
[c] Reaction performed under ultrasonication with irradiation frequency 30 kHz and ultrasonic power 100 W at RT 30°C.
[d] Reaction performed under ultrasonication with irradiation frequency 40 kHz and ultrasonic power 100 W at RT 30°C.
[e] Isolated yield

Initially, the model reaction was run in water under stirring for 24 h at RT, but no formation of desired product indolo[2,1-*b*]quinazoline-6,12-dione **3a** was observed by TLC (Table I, entry 1). It might be due to the insolubility of substrates in water. Then the model reaction was run in solvents like ethanol (EtOH), methanol (MeOH), dichloromethane (DCM), dimethyl formamide (DMF) and acetonitrile (ACN) at RT for 24 h and noticed 24-40% product yield (Table I, entries 2–6). But relatively better yield (52%) of product **3a** was obtained in tetrahydrofuran (THF) within 24 h of stirring at RT (Table I, entry 7). These results clearly demonstrated that the reaction rate was influenced by solvent. Baker's yeast is a known source of extracellular enzymes and ultrasonication has been used to disrupt the cells of baker's yeast for fast release of enzymes. So we thought that fast release of enzymes of baker's yeast after ultrasonication could increase the rate of reaction as enzyme catalytic promiscuity has already been exploited in organic synthesis[45]. Therefore, we have carried out the model reaction in different solvents under ultrasonic irradiation and it was noted that the shortest reaction time and best yield were obtained in THF under ultrasonication (88%, Table I, entry 7). In view of these observations we have selected THF as the reaction medium for baker's yeast catalyzed synthesis of indolo[2,1-*b*]quinazoline-6,12-diones under ultrasonic irradiation.

Table II — Study of catalyst efficiency for the synthesis of indolo[2,1-*b*]quinazoline-6,12-dione [a]

Entry	Amount of catalyst (mg)	Reaction Time [b] (h)	Yield [c] (%)
1	100	3	68
2	200	3	78
3	300	3	82
4	400	3	88
5	500	3	88

[a] Reaction conditions: isatoic anhydride (1 mmol), isatin (1 mmol), solvent 5 mL under sonic condition with irradiation frequency 30 kHz and at RT (30°C).
[b] Reaction progress monitored by TLC.
[c] Isolated yield.

Thereafter, we investigated the effect of amount of baker's yeast on the yield of desired product **3a** (Table II entries 1–5). Initially the model reaction was run using 100 mg of yeast and noticed 68% product formation after 3 h of ultrasonication. Therefore, the amount of yeast was increased to 200 mg, 300 mg, 400 mg and 500 mg and it was observed that 400 mg

of baker's yeast gave maximum yield (88%) of product **3a**. By increasing the amount of baker's yeast, number of active sites of enzymes (released from yeast due to ultrasonication) that took part in reaction would increase, consequently the rate of reaction increased.

In order to understand the effect of sonication frequency on the yield of reaction, model reaction was run under two different frequencies of ultrasound *viz.* 30 kHz and 40 kHz at RT. It was observed that the reaction yield was not affected to a considerable extent with increase in irradiation frequency from 30 kHz (88%, Table I, entry 7) to 40 kHz (86%, Table I, entry 8). Therefore, the synthesis of indolo[2,1-*b*]quinazoline-6,12-dione at the frequency of 30 kHz at RT was found to be very effective.

It was then decided to examine the synergetic effect of baker's yeast and ultrasonication on the synthesis of indolo[2,1-*b*]quinazoline-6,12-dione, and the results of different experiments are summarized in Figure 2.

When the model reaction was run in THF in absence of baker's yeast at RT (Figure 2, Reaction condition 1), only a trace yield of product **3a** was observed even after stirring for 24 h. However, when the reaction was carried out with baker's yeast in THF at RT, the yield of product was found to increase to 52% (Figure 2, Reaction condition 2, Table I, entry 7). After that, we ran the model reaction without yeast in THF under ultrasonication for 6 h and noticed 20% of product yield (Figure 2, Reaction condition 3). Therefore, it was concluded that the absence of baker's yeast strongly affects the reaction outcome with and without ultrasonication. Next, we have performed the reaction with baker's yeast

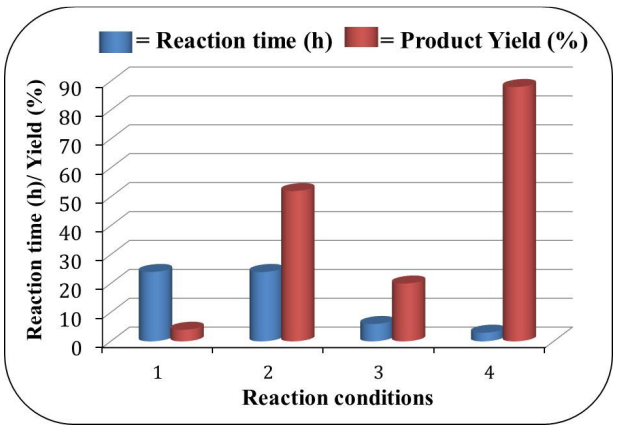


Figure 2 — Study of synergetic effect of baker's yeast and ultrasonication

under ultrasonication in THF at RT and observed 88% of product yield (Figure 2, Reaction condition 4). Therefore, it was concluded that in the present system baker's yeast as well as ultrasound, both are essential for the synthesis of title compounds.

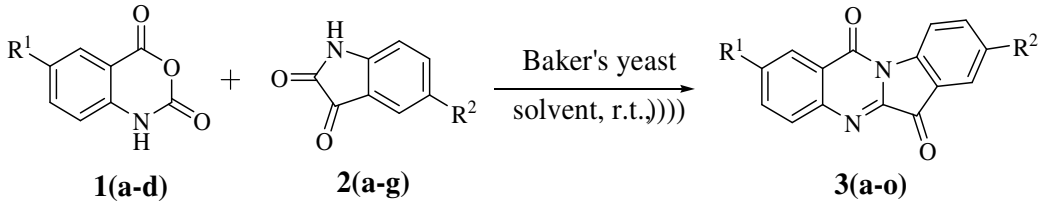
To explore the scope and feasibility of the method, a series of indolo[2,1-*b*]quinazoline-6,12-diones were synthesized using baker's yeast in THF at RT under ultrasonication. The results in Table III (Entries 1–15) demonstrated that the protocol could be applied to various substituted isatoic anhydrides and substituted isatins with satisfying yields. It is noteworthy that the electronic nature of substituents of isatoic anhydrides and isatins has no distinct effect on product yield.

The mechanism of the pyrazole formation is conceptualized in Figure 3. On disruption of cells of baker's yeast after ultrasonication, various enzymes are found to be available, displaying specific catalytic behaviors. These released enzymes have sites of poly-activations[7]. These sites might be activating the carbonyl carbon at position 2 of the isatoic anhydride **1a** for nucleophilic attack by isatin **2a**, leading to cleavage of the anhydride ring and formation of the intermediate **A**. The intermediate A, then reacts at position 2 of isatin to form the product **3a**. When the model reaction was run by employing inactivated baker's yeast (inactivation was carried out by boiling yeast in water and dead cells obtained after centrifugation were used as a catalyst), no formation of product was noticed. Due to thermal inactivation of baker's yeast, enzymes are inactivated. It indicates that, components apart from enzymes present in baker's yeast are not responsible to catalyze reaction of isatin with isatoic anhydride. Therefore, we believe that the enzymes present in baker's yeast are accelerating the reaction between isatoic anhydrides and isatins leading to the desired indolo[2,1-*b*]quinazoline-6,12-diones.

Materials and Methods

The various substrates used in the present study were sourced from Sigma Aldrich and Alfa Aesar in high purity. Thin-layer chromatography was carried out using silica gel G 60 F_{254} plates (Merck), visualized with ultraviolet light. The melting points of products were measured in open capillary tubes and are uncorrected. Infrared spectra were recorded as KBr pellets on Perkin-Elmer FT-IR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Brucker-Avance 300 MHz spectrometer with tetramethylsilane as internal standard. Mass spectra

Table III — Baker's yeast mediated synthesis of indolo[2,1-*b*]quinazoline-6,12-diones under ultrasonic irradiation [a]



1(a-d) **2(a-g)** **3(a-o)**

Entry	R^1	R^2	Product	Time (h)	Yield[b] (%)	m.p. (°C)
1	H	H	**3a**	3.0	88	272[38]
2	H	OCH_3	**3b**	3.0	90	268[38]
3	H	NO_2	**3c**	4.5	88	258[25]
4	H	Cl	**3d**	3.0	92	294[38]
5	H	Br	**3e**	3.0	91	292[38]
6	H	F	**3f**	3.5	89	262[25]
7	H	CH_3	**3g**	4.0	91	280[38]
8	OCH_3	OCH_3	**3h**	3.0	90	281[38]
9	OCH_3	CH_3	**3i**	3.0	89	292[38]
10	Br	CH_3	**3j**	3.0	92	>310[38]
11	Br	NO_2	**3k**	4.5	89	298[25]
12	Br	Br	**3l**	3.5	94	>310[38]
13	Cl	OCH_3	**3m**	3.0	93	274[25]
14	Cl	CH_3	**3n**	3.0	90	258[25]
15	Cl	Cl	**3o**	3.0	93	290[38]

[a] Reaction conditions: isatoic anhydride (1 mmol), isatin (1 mmol), baker's yeast (400 mg) and THF(5 mL) under ultrasonic irradiation at RT (30°C).
[b] Isolated yield.

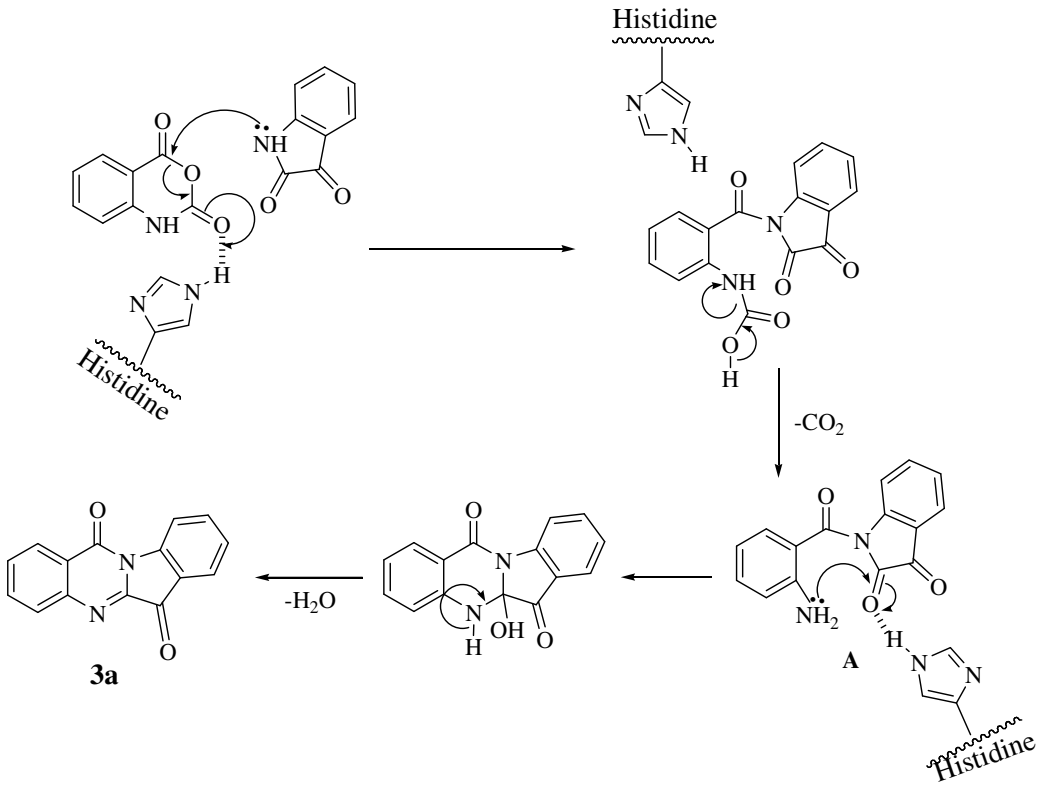


Figure 3 — Mechanistic picture of indolo[2,1-*b*]quinazoline-6,12-dione formation

were recorded on Shimadzu QP 2010 GCMS. Baker's yeast was purchased from local market. Sonication was performed in SPECTRALAB-UCB-30 ultrasonic bath with a frequency of 30 kHz and a nominal power of 100 W. The reaction flask was located in the maximum energy area in the water bath. The reaction temperature was controlled at 30°C by addition or removal of water from ultrasonic bath.

Experimental Section

Ultrasound-promoted synthesis of indolo[2,1-b] quinazoline-6,12-dione

To the solution of isatoic anhydride (1.0 mmol) and isatin (1.0 mmol) in THF (5 mL), baker's yeast (400 mg) was added. Then the reaction mixture was sonicated at 30 kHz for stipulated time mentioned in Table III at 30°C. The progress of the reaction was monitored by thin layer chromatography by using petroleum ether:ethyl acetate (7:3) as solvent system. After completion of the reaction, it was extracted with ethyl acetate and finally dried over anhydrous sodium sulphate. The resulting crude product was purified by column chromatography to afford pure indolo[2,1-*b*]quinazoline-6,12-dione.

Indolo[2,1-*b*]quinazoline-6,12-dione, 3a: Yellow solid. m.p.272°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (d, J = 8.1 Hz, 1H), 8.46 (d, J = 6.6 Hz, 1H), 8.06 (dd, J = 8.1 Hz, J = 0.6 Hz, 1H), 7.94 (dd, J = 7.8 Hz, J = 0.9 Hz, 1H), 7.90–7.84 (m, 1H), 7.83–7.78 (m, 1H), 7.72–7.67 (m, 1H), 7.47–7.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.5, 158.1, 146.6, 146.3, 138.2, 135.1, 130.7, 130.2, 127.5, 127.1, 125.4, 123.7, 121.9, 117.9; EI-MS: Calcd for $C_{15}H_8N_2O_2$: 248. Found: 248 (M^+).

8-Chloroindolo[2,1-*b*]quinazoline-6,12-dione, 3d: Yellow solid. m.p.294°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (d, J = 8.7 Hz, 1H), 8.46 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H), 8.06 (d, J = 7.2 Hz, 1H), 7.92–7.86 (m, 2H), 7.78–7.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.1, 166.1, 160.0, 146.5, 135.2, 130.8, 130.5, 127.5, 124.9, 124.6, 123.7, 119.7, 119.6, 112.2, 111.8; EI-MS: Calcd for $C_{15}H_7ClN_2O_2$: 282. Found: 282 (M^+).

8-Bromoindolo[2,1-*b*]quinazoline-6,12-dione, 3e: Brown solid. m.p.292°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (d, J = 9.3 Hz, 1H), 8.31 (d, J = 7.8 Hz, 1H), 8.03 (dd, J = 6.9 Hz, J = 2.1 Hz, 2H), 7.95 (d, J = 3.6 Hz, 2H), 7.77–7.72 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.7, 158.9, 145.9, 144.3, 140.2, 134.8, 134.1, 130.2, 129.6, 128.2, 127.2, 122.6, 122.4, 120.6, 119.4; EI-MS: Calcd for $C_{15}H_7BrN_2O_2$: 325. Found: 328 (M^+).

8-Fluoroindolo[2,1-*b*]quinazoline-6,12-dione, 3f: Yellow solid. m.p.262°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (dd, J = 9.0 Hz, J = 4.2 Hz, 1H), 8.46 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 7.8 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.60 (dd, J = 6.3 Hz, J = 2.4 Hz, 1H), 7.54–7.47 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.9, 181.8, 175.9, 173.3, 169.8, 162.0, 150.5, 138.2, 135.6, 133.6, 130.9, 127.6, 119.2; EI-MS: Calcd for $C_{15}H_7FN_2O_2$: 266. Found: 266 (M^+).

Conclusion

In conclusion, for the first time we have explored the potential of baker's yeast as whole cell biocatalyst to accelerate the synthesis of biologically active natural product tryptanthrins in organic medium. Baker's yeast is an easily available natural source of biocatalyst, inexpensive and biodegradable, making the protocol cost effective and eco-friendly. The role of ultrasound in the rate expediting of the biocatalyzed reaction is highlighted. The described methodology is applicable to a wide range of substrates and has a high functional group tolerance. Furthermore, the developed strategy accommodates the use of material and energy inputs that are inherently non-hazardous and less harmful to human being as well as environment and promotes the synthesis of structurally diverse bioactive molecules.

Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/60.

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