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An efficient practical chemo-enzymatic protocol for the synthesis of pyrazoles in aqueous medium at ambient temperature

Ananda Mane, Prabha Salokhe, Pallavi More, Rajashri Salunkhe*

Department of Chemistry, Shivaji University, Kolhapur 416004, M.S., India

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ABSTRACT

An expeditious oxidative cyclocondensation reaction of hydrazines/hydrazides with 1,3-dicarbonyl compound was efficiently developed in aqueous medium using *Saccharomyces cerevisae* (baker's yeast) as a whole cell biocatalyst at room temperature. The method has been assigned using green chemistry measures and found to give a range of N-substituted pyrazoles with moderate to excellent yields (70–92%). The reaction progress was monitored by gas chromatography.

1. Introduction

It is widely accredited that there is an increasing importance for more environmentally viable synthetic routes in organic synthesis. This progressive development known as 'Sustainable Technology' necessitates a change in scenario from traditional concepts of process efficiency to more economic and greener approaches [1]. In recent years, water as reaction medium has captured high priority as green media because it is safe to handle, environment-friendly, easily available, and enhances the reactivity and selectivity of reactions [2]. In this context, use of biocatalysts in aqueous media has emerged as a green synthetic strategy, to construct structurally diverse scaffolds from simple molecules. Biocatalysis highlights an effective and preferable alternative to the standard synthesis of potent chemicals as they can accept un-natural compounds as substrates. As whole-cell biocatalysts regenerate their own respective cofactors, they are frequently more advantages than isolated enzymes [3]. Among the various possible biocatalysts, baker's yeast (*Saccharomyces cerevisae*) is renowned catalyst, due to its low cost, easy handling, high bioavailability, and its growth does not require the assistance of a specialist in microbiology [4]. Baker's yeast projects better catalytic behaviour in aqueous medium [5] and has the ability to accelerate the transformations under mild reaction conditions such as temperature, light, stirring etc. [6] and is known to play vital role in various organic transformations [5,7]. Baker's yeast has been extensively used in the synthesis of library of heterocyclic compounds [8] such as, benzimidazoles, quinoxalines, polyhydroquinolines, 4H-pyranes, 1,4-dihydropyridines, 3,4-dihydro-pyrimidine-2-(1H)-ones, isoindolo[2,1-a]quinazolines, 1,4-benzothiazines etc. Recently Singh et al. [9] reported the synthesis of indolyl chromenes and bisindolyl alkanes in water using baker's yeast as the catalyst.

Pyrazole derivatives constitute the core structure of naturally occurring and biologically active heterocyclic compounds. Pyrazole nucleus containing compounds represent important building blocks for luminophores, dyes, insecto-acaricides, antibacterial, antidepressant, analgesic and antiphlogistic drugs [10]. Pyrazole derivatives are of great interest due to their pharmacological properties for instance, pyrazole diimide (Fig. 1, I) acts as anticancer drug [11]. Celecoxib {4-[5-(methylphenyl)-3-trifluoromethyl) pyrazol-1-yl] benzene sulphonamide} (Fig. 1, II) acts as inhibitor of cyclo-oxygenase-2 (COX-2) and reduces side effects in the gastrointestinal tract [12]. Methylthiopyrazole epothilone B (Fig. 1, III) shows strong antitumor activity through the stabilisation of microtubules by binding with tubulin [13]. Due to unique biological activities of pyrazole derivatives in medicinal chemistry, the development of elegant and efficient ways enabling facile access to this heterocycle is desirable.

In recent years, a large number of protocols [14] for preparation of pyrazoles have been developed in different ways using polystyrene supported sulfonic acid (PSSA) [15], Al_2O_3/clay (montmorillonite K10) [16], Amberlyst-70 [17], polymer bound-*p*-toluene sulphonic acid (PTSA) [18], silica supported sulphuric acid ($H_2SO_4{\cdot}SiO_2$) [19], $Sc(OTf)_3$ [20], Zn[(L)-proline]$_2$ [21], sulphamic

* Corresponding author.
E-mail address: rsschem1@gmail.com (R. Salunkhe).

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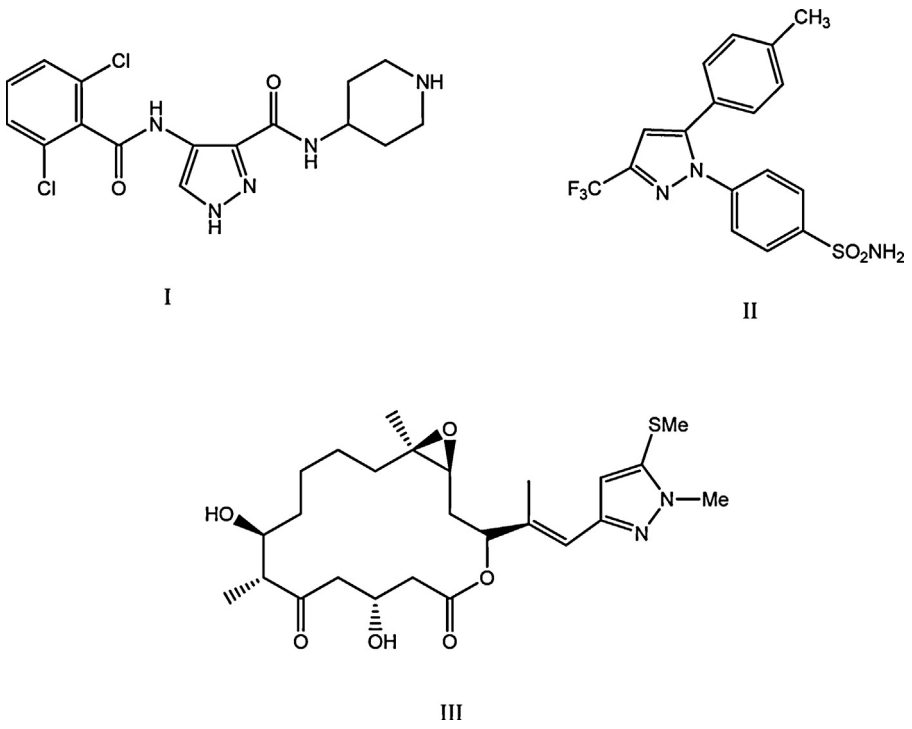


Fig. 1. Biologically active compounds containing pyrazole as a core structure.

acid [22] as catalysts. These reported methodologies produced good results in many instances. However most of the methods reported suffer from certain limitations such as use of expensive reagents, tedious procedure for preparation of catalysts, low selectivity, generation of acidic and metallic waste and tedious workup conditions. Hence, the development of an efficient, simple, easy workup and environmentally benign protocol using green solvent for the construction of pyrazole derivatives is of significant interest. In view of the above valid points, we disclose herein an environmentally benign and effective protocol for the synthesis of pyrazole derivatives employing baker's yeast (*S. cerevisae*) in fermenting medium at an ambient temperature. To the best of our knowledge, the role of baker's yeast in the cyclocondensation of hydrazines/hydrazides and 1, 3-diketones has not been previously reported.

2. Experimental

2.1. Materials and instruments

Solvents and reagents involved in the synthesis were sourced from commercial suppliers and used as such. Progress of all reactions and purity of dicarbonyl compound, hydrazines and hydrazides were monitored by thin layer chromatography (TLC) carried out on silica gel G 60 F_{254}plates (Merck). Chromatograms were developed using petroleum ether: ethyl acetate (7:3) as solvent system. The melting points of products were measured in open capillary tubes and are uncorrected. GC analysis was performed using a 25 m HP-5 column (crosslinked 5% PH ME Siloxane) with an inner diameter of 0.25 mm and a film thickness of 0.25 m. GC was operated using a temperature profile with a starting temperature of 40 °C, then increased by 15 °C/min to an end temperature of 300 °C Infrared spectra were recorded on Perkin Elmer FT-IR spectrometer. The ^{1}H and ^{13}CNMR spectra were recorded on a Brucker-Avance 300 MHz spectrometer using TMS as an internal standard and $CDCl_3$ as a solvent. Mass spectra were recorded on Shimadzu QP 2010 GCMS. Baker's yeast was purchased from local market.

2.2. Experimental procedure

2.2.1. Fermentation of baker's yeast

In a round bottom flask containing 5 mL of 0.01 M phosphate buffer (pH 7.0), bakers' yeast (400 mg) and D-glucose (750 mg) were added and resulting solution was stirred for 12 h at 32 °C for fermentation.

2.2.2. Synthesis of pyrazoles

To the fermented baker's yeast 1,3-dicarbonyl compound (1 mmol) and hydrazine/hydrazide (1.2 mmol) were added and the reaction mixture was stirred at room temperature for indicated time (Table 1). The progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, it was extracted with dichloromethane and finally dried over anhydrous sodium sulphate. The organic layer was concentrated in vacuo. The resulting crude product was purified by column chromatography using petroleum ether:ethyl acetate (7:3) as eluent.

Table 1
Effect of amount of catalyst on the reaction of acetyl acetone and phenyl hydrazine.[a]

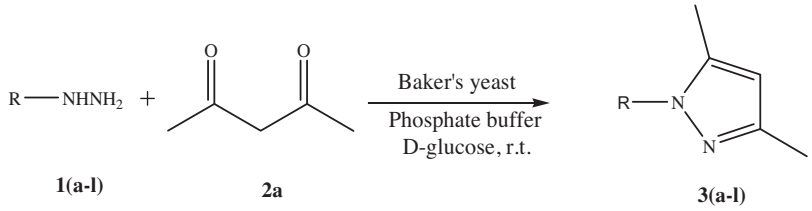
Entry	Amount of catalyst (mg)	Reaction time[b] (h)	Yield (%)[c]
1	100	00:15	78
2	200	00:15	83
3	300	00:15	85
4	**400**	**00:15**	**92**
5	500	00:15	89

Bold values mean that at 400 mg of catalyst yield of product is maximum.

[a] Reaction conditions: acetyl acetone (1 mmol), phenyl hydrazine (1.2 mmol), D-glucose, phosphate buffer (pH 7.0, 5 mL) at room temperature.

[b] Reaction progress monitored by TLC.

[c] Isolated yield.



Scheme 1. Reaction of different hydrazines/hydrazides with 1,3-dicarbonyl compound in fermented baker's yeast at room temperature (**3a–3l**).

2.3. Spectral data for representative compounds

2.3.1. (4-Chlorophenyl)(3,5-dimethyl-1H-pyrazol-1-yl) methanone (**3**)

Oil; IR (KBr): ν = 3110, 2930, 1698, 1582, 1342, 1081, 910 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3H), 2.54 (s, 3H), 6.04 (s, 1H), 7.44 (d, J = 1.8, 6.6 Hz, 2H), 7.97 (dd, J = 1.8, 6.6 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 14.3, 111.2, 128.0, 131.5, 132.3, 138.7, 145.8, 152.3, 166.9 ppm. MS (EI): m/z = 234 (M^+).

2.3.2. (4-Nitrophenyl)(3,5-dimethyl-1H-pyrazol-1-yl) methanone (**8**)

Yellow solid; IR (KBr): ν = 3060, 2850, 1620, 1562, 1340, 1071, 940 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 2.52 (s, 3H), 6.19 (s, 1H), 8.38 (d, J = 1.8, 6.9 Hz, 2H), 8.77 (dd, J = 1.8, 6.6 Hz, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 15.7, 112.3, 129.1, 133.5, 136.3, 140.7, 151.8, 158.3, 169.9 ppm. MS (EI): m/z = 245 (M^+).

2.3.3. 1-(3,5-Dimethyl-1H-pyrazol-1-yl)-2-(3-methylphenyl-oxy) ethanone (**10**)

White solid; IR (KBr): ν = 3001, 2920, 2840, 1742, 1610, 1571, 1398, 1328, 1250, 1161, 1090, 964, 839, 774 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 2.35 (s, 3H), 2.59 (s, 3H), 5.37 (s, 2H), 5.98 (s, 1H), 6.75–6.80 (m, 3H), 7.12–7.18 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 14.1, 21.5, 66.5, 110.9, 111.5, 116.0, 122.5, 128.3, 139.0, 144.2, 152.3, 158.1, 167.9 ppm. MS (EI): m/z = 244 (M^+).

3. Results and discussion

Herein, we report an efficient and economical protocol for the synthesis of pyrazoles. The protocol involves the oxidative cyclocondensation of hydrazines/hydrazides with 1,3-dicarbonyl compounds, catalysed by baker's yeast as a whole cell biocatalyst at room temperature.

3.1. Baker's yeast mediated synthesis of pyrazoles

To establish the optimal reaction conditions, we have carried out different experiments as follows; **(I)** *control experiment:* a control reaction was carried out using acetyl acetone (1 mmol) and phenyl hydrazine (1.2 mmol) in 5 mL of 0.01 M phosphate buffer (pH = 7) and D-glucose (Scheme 1). The reaction mixture was stirred at room temperature for 24 h, after workup and purification of crude mixture by column chromatography only 8% of 1-phenyl-3,5-dimethyl pyrazole (**3a**) was obtained. (II) *with dry yeast*: baker's yeast, D-glucose (750 mg), acetyl acetone (1 mmol) and phenyl hydrazine (1.2 mmol) were taken together in 0.01 M phosphate buffer (5 mL, pH = 7) and stirred. After workup and purification, 44% of 1-phenyl-3,5-dimethyl pyrazole (3a) was obtained. (III) *with fermented yeast:* baker's yeast (400 mg) and D-glucose (750 mg) were taken in 5 mL of 0.01 M phosphate buffer and stirred for 12 h at room temperature for fermentation. Acetyl acetone (1 mmol) and phenyl hydrazine (1.2 mmol) were added to the fermented yeast. Surprisingly the yield of product (**3a**) was increased to 90% after stirring the reaction mixture for only 15 min at room temperature. (IV) *with yeast extract*: we also carried out a experiment in which, baker's yeast was stirred in distilled water and supernatant solution thus obtained after centrifugation was used as yeast extract in place of fermented baker's yeast for the model reaction. It was observed that 1-phenyl-3,5-dimethyl pyrazole (**3a**) was formed in 20% yield after stirring reaction mixture for 24 h. (V) *with inactive yeast*: the model reaction was also run by employing inactivated baker's yeast (inactivation was carried out by boiling yeast in water and dead cells obtained after centrifugation were used instead of active baker's yeast) as a catalyst. After 24 h stirring of reaction mixture only 8% yield of product (**3a**) was isolated. Thus it was concluded that fermented baker's yeast plays a crucial role in efficient cyclocondensation of hydrazines/hydrazides and 1,3-diketones. It is also clear that addition of components (acetyl acetone and phenyl hydrazine) to fermented yeast (experiment III) gives a good yield in comparison to that in which all the components were added simultaneously (experiment II).

Table 2
Baker's yeast catalysed synthesis of pyrazoles (**3a–3l**) at room temperature.[a]

Entry	*R*	Reaction time (h)	Product	M. P. (°C)	Yield (%)[b]
1	C_6H_5	00:15	**3a**	Oil [23a]	92
2	C_6H_5—CO	00:30	**3b**	228–230 [24a]	87
3	4-Cl—C_6H_5—CO	00:40	**3c**	Oil [24a]	82
4	2-Cl—C_6H_5—CO	01:20	**3d**	Oil [23b]	80
5	2-Br—C_6H_5—CO	01:30	**3e**	52–55 [24a]	78
6	3-C_5H_4N—CO	00:30	**3f**	152–154 [24b]	77
7	4-C_5H_4N—CO	00:50	**3g**	Oil [24a]	83
8	4-NO_2—C_6H_5—CO	08:00	**3h**	134 [24a]	77
9	2,4—NO_2—C_6H_5	24:00	**3i**	119–121 [20]	75
10	3-Me—C_6H_5—OCH_2CO	00:40	**3j**	50–52 [24a]	84
11	H	00:10	**3k**	106–108 [23a]	90
12	CH_3CO	00:25	**3l**	Oil [20]	90

[a] Reaction conditions: acetyl acetone (1 mmol), hydrazine/hydrazide (1.2 mmol), baker's yeast (400 mg), D-glucose (750 mg), phosphate buffer (pH 7.0, 5 mL) at room temperature.
[b] Isolated (molar) yield after column chromatography.

The effect of amount of biocatalyst on the reaction of acetyl acetone with phenyl hydrazine was studied and results are summarised in Table 1. It was observed that the 400 mg of catalyst was sufficient for the condensation of acetyl acetone and phenyl hydrazine to give 1-phenyl-3,5-dimethyl pyrazole (3a) within 15 min (Table 1, entry 4).

To delineate optimised reaction conditions, the methodology was evaluated by using several structurally diverse, activated and deactivated hydrazines/hydrazides. A series of pyrazole derivatives was synthesised and results are recorded in Table 2 . From these results it seems that baker's yeast accepts broad array of substrate combinations. The reaction time and reaction yield indicates that electronic effects of substituent's on hydrazine and hydrazide components play a greater role in these reactions. The pyrazole formation reaction proceeds smoothly with phenyl hydrazine (entry 1) and hydrazine hydrate (entry 11) with 90–92% yield in short time. Whereas slightly electron donating substituent's on hydrazides (entries 2–5) provides pyrazole products smoothly, electron demanding hydrazide (entry 8) required more time for product formation. In addition with respect to the substituent's on hydrazide component, it was observed that steric effects are important. In the case of 4-chlorobenzhydrazide 40 min of stirring was required to give desired product **(entry 3),** whereas in the case of 2-chlorobenzohydrazide the pyrazole formation reaction

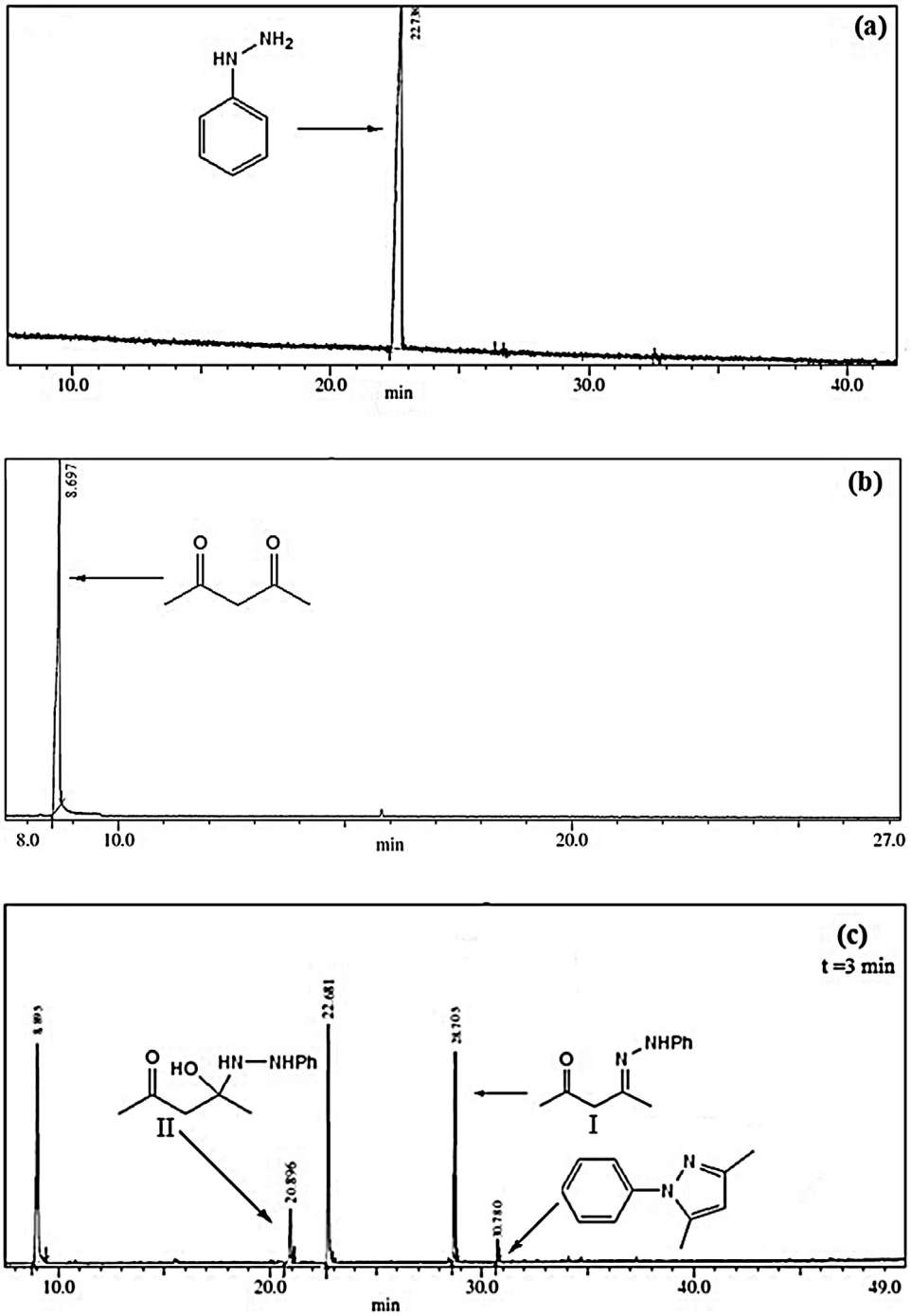


Fig. 2. Progress of pyrazole formation as monitored by gas chromatography at different time intervals. Gas chromatograms of: (a) phenyl hydrazine, (b) acetyl acetone, (c) aliquot of reaction mixture after 3 min, (d) ~ after 6 min (e) ~ after 9 min (f) ~ after 15 min.

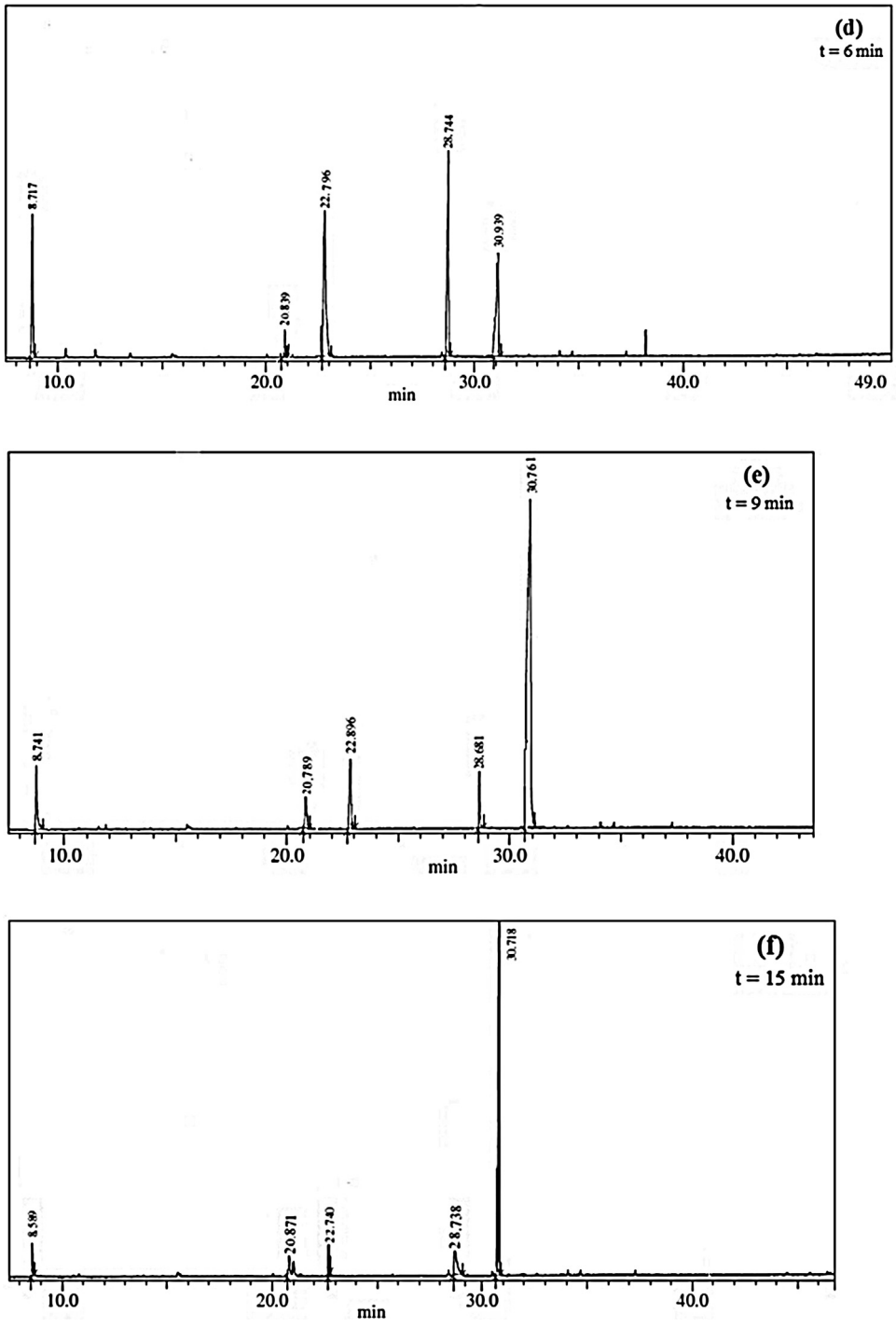


Fig. 2. (*Continued*).

was completed in 80 min (**entry 4**). Hydrazide with bromo substituent at ortho- position, requires more time to complete the reaction with slight decrease in yield as compared to hydrazide with chloro substituent at ortho- position (**entries 4 and 5**) As the bulk of R group increases, the reaction requires more time. With 4-nitrobenzohydrazide and 2,4-dinitrophenylhydrazine the pyrazole formation reaction requires 8 h and 24 h respectively (entries 8 and 9). In the absence of the catalyst 2,4-dinitrophenyl hydrazine does not form pyrazole even at 80 °C, but it gave satisfactory yield in the presence of baker's yeast (entry 9). The yield of pyrazole was found to be good when 2-(*m*-tolyloxy) acetohydrazide was reacted with 1,3-dicarbonyl compound (entry 10). This is because *m*-tolyloxy group is far away from reaction site resulting in less steric interaction. Acetohydrazide was also found to afford *N*-acetyl pyrazole in excellent yield (entry 12). Heteroaryl hydrazides, pyridine-3-carbohydrazide and pyridine-4-carbohydrazide has also been successfully condensed with 1,3-dicarbonyl compound in the presence of baker's yeast to respective pyrazoles with 75–85% yield (entries 6 and 7). The above results suggest that electron density of hydrazines and hydrazides is essential for the success of pyrazole formation reaction.

The formation of desired products (Table 2, entries 1–12) was confirmed from IR, ^{1}HNMR, ^{13}CNMR spectra as well as by mass spectroscopy and in accordance with literature. The ^{1}HNMR of each

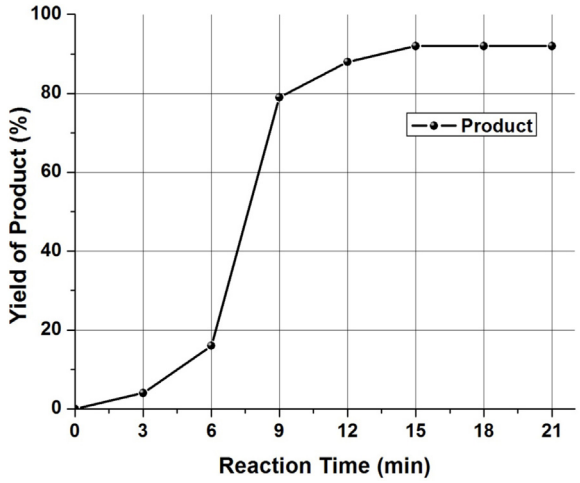


Fig. 3. Product formation-time dependences for the condensation of acetyl acetone and phenyl hydrazine in fermented baker's yeast.

product exhibited a singlet in the range δ = 5.98–6.19 ppm due to —CH of the pyrazole ring. In IR spectra, existence of a strong intensity peak in the range 1560–1600 cm^{-1} due to C=N functionality, indicates the complete conversion of hydrazines/hydrazides to corresponding pyrazoles.

To explore the potential value of fermented baker's yeast as catalytic system, a scaled-up version was performed. By treatment of 6 mmol of phenyl hydrazine with 5 mmol 1, 3-dicarbonyl compounds under the optimal reaction conditions, desired product was produced in 88% yield.

3.2. Kinetic study of pyrazole formation

The reaction progress for the condensation of compounds **1a** and **2a** catalysed by fermented baker's yeast (Scheme 1) was conveniently monitored by gas chromatography. Aliquots of reaction mixture were collected at different time intervals, extracted with dichloromethane and analysed by gas chromatography {Fig. 2(c–f)}. Chromatograms of substrates are shown by Fig. 2a and b. The peak at 22.738 min in Fig. 2a is due to phenyl hydrazine and the peak at 8.697 min in Fig. 2b is due to acetyl acetone. Gas chromatograms in Fig. 2(c–f) depicting the progress of reaction. After 3 min of stirring of reaction mixture, we observed the peak at 28.705 min due to phenyl hydrazone intermediate (II) and a peak at 20.896 min due to small quantity carbinolamine intermediate (I) but we did not observed the peak due to pyrazoline intermediate. This might be because of unstability of pyrazoline under GC conditions (Fig. 2c). After 9 min formation of pyrazole was observed due to rapid loss of intermediate I (Fig. 2e). Further we stirred the reaction mixture to 15 min and observed the maximum conversion of reactants into product. After 15 min, we found that there is no noticeable increase in yield of product.

The rate of pyrazole formation (Scheme 1, entry 1) at different time intervals in terms of yield is summarised in Fig. 3. Up to 6 min of stirring, only ~16% of the product was obtained, after which rate of reaction increases leading to ~79% pyrazole formation within 9 min. After 12 min we observed ~88% product and then it was increased to ~92% at 15 min. Further increase in reaction time has no effect on yield of product.

3.3. Role of baker's yeast

Baker's yeast produces variety of enzymes during fermentation [25,26]. Among them, lipase is known to catalyse cyclocondensation reactions [27] and is widely employed in organic synthesis. In particular, amino acid residues like histidine, serine and aspartate or glutamate enhances electrophilicity of carbonyl carbon of 1, 3-dicarbonyl compound by forming 1, 3-dicarbonyl: enzyme noncovalent complexes [27,28]. When the reaction was run by employing thermally inactivated baker's yeast (inactivation was carried out by boiling yeast in water) as a catalyst, the yield of 1-phenyl-3,5-dimethyl pyrazole was 8%, but with active baker's yeast yield was increased up to 92%. Due to thermal inactivation of baker's yeast lipase is inactivated which results in lower yield of product. It indicates that, components apart from enzymes present in baker's yeast are not responsible to catalyse reaction of hydrazines/hydrazides with 1, 3-dicarbonyl compound. We have also carried out a reaction by employing isolated lipase from *S. cerevisae* as a catalyst and obtained 1-phenyl-3,5-dimethyl pyrazole with 60% yield. Therefore we believe that the enzyme lipase available in baker's yeast is likely to be responsible to accelerate the addition of hydrazines/hydrazides on 1, 3-dicarbonyl compound leading to the desired pyrazole derivatives.

4. Conclusion

We have reported for first time the use of baker's yeast as whole cell biocatalyst to accelerate the synthesis of pyrazole derivatives. The biocatalyst is inexpensive, easily available and biodegradable making the protocol cost effective and ecofriendly. Furthermore, the described procedure allows general synthesis of inaccessible pyrazoles offering attractive features such as ambient reaction conditions, operational simplicity, clean reaction profile and tolerance of wide variety of functional groups. Ongoing studies are focused on applying this strategy to synthesise more complex molecules.

Acknowledgements

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