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First time reported enzymatic synthesis of new series of quinoxalines—A green approach

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ABSTRACT

New series of quinoxaline derivatives have been efficiently synthesized using environment friendly catalyst, i.e. enzyme. This methodology provides an alternative safest route for the synthesis of quinoxalines. Dihydroxy benzenes were used for the first time in the synthesis of quinoxalines.

1. Introduction

The discovery of efficient, simple and straightforward environmental benign processes and methodologies for the synthesis of widely used organic compounds from readily available reagent is one of the major challenges for chemist in organic synthesis. Quinoxaline derivatives are the subject of considerable interest from both academic and industrial perspectives because they are significant intermediates for the manufacturing of pharmaceutical and advanced materials [1]. Despite remarkable efforts in last decades [2], challenges remain unfold for the sustainable greener procedure for the synthesis of quinoxaline ring.

Use of naturally occurring substances as a catalyst can fulfil the major requirements of green chemistry. The main area is enzyme catalysed reactions [3–9]. Oxidative transformation becomes more attractive if aerial oxygen could be used as an oxidant. Laccases are multicopper oxidases which are able to abstract hydrogen from phenolic hydroxyl groups by using molecular oxygen as an electron acceptor, resulting in phenoxy radical that undergo broad range of reactions [10–17].

The high oxidative selectivity exhibited by laccase in aqueous solution has made them attractive for a variety of oxidations and coupling reactions in green chemistry.

Few methods for the preparation of quinoxalines have been developed involving condensation of 1,2-diamines with 1,10-phenanthroline-5,6-dione[18], α-diketones [19], β-catalysed oxidative coupling [20], microwave[21], and the use of $RuCl_2(PPh_3)_3$–TEMPO [22], MnO_2 [23], $POCl_3$ [24], iodine [25], CAN [26], etc.

To the best of our knowledge, there is no report on the synthesis of such compounds via efficient and simple enzymatic procedure. Moreover dihydroxy benzene has never been involved in quinoxaline synthesis via chemical method. It is shown that aminoquinone derivatives are obtained from the reactions of quinones and the ordinary amines (primary and secondary). When the steric hindrance is absent, two molecules of amine add to the quinone, while in the presence of steric hindrance, only one molecule will be added [27]. As the part of green research laboratory our goal is to explore such type of reactions, which could be performed under mild conditions [28–30]. Hence herein we are first time reporting laccase catalysed oxidative coupling of dihydroxy benzene (catechol, 1,4-hydroquinone) and diamines.

2. Experimental

N,N′-dimethylethylenediamine, and various dihydroxy benzene were purchased from Aldrich. Guaiacol was purchased from Hi Media Laboratories Pvt. Ltd. (Mumbai, India). Q-sepharose was purchased from Sigma (St. Louis, USA). All media components and chemicals used were of analytical grade.

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2.1. Microorganisms

The laccase producing *Ganoderma* sp. rckk-02 was obtained from Lignocellulose Biotechnology Laboratory, University of Delhi, South Campus, New Delhi. The fungal cultures was grown and maintained on malt extract agar (MEA) containing g/L: malt extract 20.0; KH_2PO_4 0.5; $MgSO_4{\cdot}7H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$ 0.5, agar 20.0 (pH 5.4) at 30 °C. Pure cultures were stored at 4 °C and subcultured every fortnight.

2.2. Laccase production

Laccase production was carried out using *Ganoderma* sp. rckk-02 under solid-state fermentation conditions. 1000 g of air dried wheat bran was spread in separately sterilized enamel trays (78 cm × 51 cm × 8.1 cm) to about 1.0 cm thick and was moistened with mineral salt solution containing g/L: KH_2PO_4 0.5; $MgSO_4{\cdot}7H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$ 0.5, agar 20.0 (pH 5.4) in 1:2 ratio of solid substrate to moisture. The trays were put in autoclavable poly bags and sterilized at 121 °C (15 psi) for 30 min. The substrate was inoculated with 0.4% (w/w) of fungal pellets of *Ganoderma* sp. rckk-02 in separate trays, respectively. The trays were incubated for 168 h at 30 ± 1 °C in a 70% relative humidity chamber. The laccase from the above three organisms was harvested by adding 0.1 mol/L citrate phosphate buffer (pH 5.4) in 1:5 ratio of solid substrate to moisture. The mixture was homogenized for 30 min at 30 °C, 200 rpm. The solid biomass residues were separated from the suspensions by filtration through muslin cloth and the filtrate obtained was centrifuged at 10,000 × *g* for 20 min at 4 °C. The supernatants obtained were used as the source of crude enzyme preparations.

2.3. Purification of laccase

The crude laccase enzyme extracts (1000 mL) *Ganoderma* sp. rckk-02 was precipitated by adding ammonium sulphate (40–80% cut off) and centrifuged at 10,000 × *g* for 20 min at 4 °C. The precipitates were resuspended in 50 mM citrate phosphate buffer (pH 5.4) and dialyzed against the same buffer. These partially purified enzyme samples 100 mL from each ungus were loaded to an anion exchange Q-Sepharose coloumn (Sigma–Aldrich, St. Louis, MO, USA) seperately, equilibrated with 10 mM Tris–HCl Buffer (pH 7.5). The proteins were eluted by NaCl gradient (0–0.5 M dissolved in equilibrating buffer) at a flow rate of 1 mL/min. with each 1 mL fraction. Fractions with laccase activity were pooled and concentrated using 10-kDa filter membrane (Vivaspin, Vivascience, Sartorious Group, Stone house, UK) at 4 °C and assayed for laccase activity.

2.4. Enzyme assay

Guaiacol was used as a substrate for assaying laccase activity. One unit of laccase was defined as the change in absorbance of 0.01 mL^{-1} min^{-1} at 470 nm [31,32].

2.5. General procedure for the synthesis of quinoxalines

A mixture containing dihydroxy benzene 2 or 4 (1 mmol), N,N′-dimethylethylenediamine 1 and laccase (200 U) in buffer solution of pH 7 were stirred at room temperature for approximately 10 h (monitored by TLC, as reported in Table 3). After completion of reaction, reaction mixture was extracted by ethylacetate. Organic phase was dried over anhydrous sodium sulphate, and evaporated; the resulting crude products were purified by silica column chromatography, using ethylacetate and hexane as an eluent. All the compounds are new and are characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy.

2.6. Spectral data of the synthesized compounds:

2.6.1. 1,4-Dimethyl-1,2,3,4-tetrahydro-quinoxaline-6,7-diol

Isolated yield: 61% M.pt; mp 164–165 °C. IR(KBr) (νmax/cm^{-1}): 3415, 3410, 2929, 1580, 1549, 1450, 1420, 1360. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.39(s, 2H, ArH) 3.52 (m, 4H, CH_2), 3.01(s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.5, 57.7, 99.9, 125.9, 138.9 Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N,14.42. Found: C, 61.40; H, 7.74; N, 14.50. ESI-MS 195.11 (M+1).

2.6.2. 1,4,5-Trimethyl-1,2,3,4-tetrahydro-quinoxaline-6,7-diol

Isolated yield: 65% M.pt; mp 149–150 °C. IR(KBr) (νmax/cm^{-1}): 3410, 3411, 2922, 1582, 1540, 1451, 1423, 1362. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.30(s, 1H, ArH) 3.49 (m, 4H, CH_2), 3.15(s, 3H, CH_3), 3.06(s, 3H, CH_3), 1.99(s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.23, 38.1, 40.1, 48.0, 49.7, 97.8, 111.10, 125.0, 125.8, 134.2, 136.1 Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.30; H, 7.70; N, 13.55. ESI-MS 209.12 (M+1).

2.6.3. 5-Methoxy-1,4-dimethyl-1,2,3,4-tetrahydro-quinoxaline-6,7-diol

Isolated yield: 60% M.pt; mp 156–157 °C. IR(KBr) (νmax/cm^{-1}): 3425, 3421, 2927, 1585, 1520, 1471, 1410, 1358, 1310, 1281, 1195, 820. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.41(s, 1H, ArH), 3.71(s, 3H, OCH_3), 3.45 (m, 4H, CH_2), 3.29(s, 3H, CH_3), 3.01(s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.5, 45.1, 48.0, 49.5, 96.9, 111.10, 125.0, 125.8, 136.2, 138.2 Anal. Calcd for $C_{11}H_{16}N_2O_3$: C, 58.91; H, 7.19; N,12.41. Found: C, 58.42; H, 7.21; N, 12.55. ESI-MS 225.12 (M+1).

2.6.4. 1,4-Dimethyl-1,2,3,4-tetrahydro-quinoxaline-5,8-diol

Isolated yield: 63% M.pt; mp 168–169 °C. IR(KBr) (νmax/cm^{-1}): 3415, 3410, 2929, 1580, 1549, 1450, 1420, 1360. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.61(s, 2H, ArH) 3.56 (m, 4H, CH_2), 2.90(s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 41.5, 60.4, 107.5, 117.9, 136.5 Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.42. Found: C, 61.51; H, 7.34; N, 14.51. ESI-MS 195.11 (M+1).

2.6.5. 1,4,6-Trimethyl-1,2,3,4-tetrahydro-quinoxaline-5,8-diol

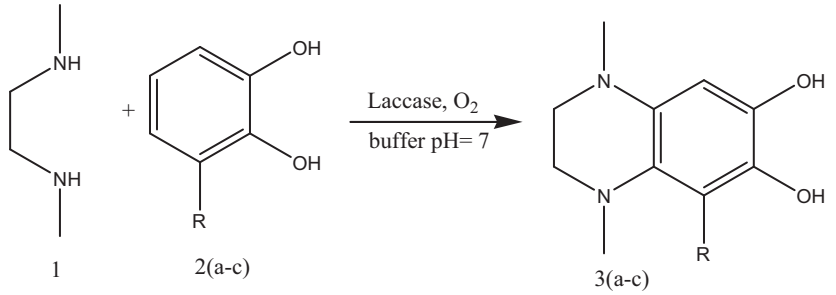
Isolated yield: 59% M.pt; mp 158–159 °C. IR(KBr) (νmax/cm^{-1}): 3413, 3411, 2921, 1581, 1528, 1473, 1416, 1377, 1316, 1105, 825, 766. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.21(s, 1H, quinone) 3.52 (m, 4H, CH_2), 3.21(s, 3H, CH_3), 3.12(s, 3H, CH_3), 2.01(s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.81, 40.3, 44.2, 48.0, 49.2, 95.3, 111.10, 125.0, 125.8, 134.2, 136.1 Anal. Calcd for $C_{11}H_{16}N_2O_2$: C, 63.44; H, 7.74; N, 13.45. Found: C, 63.39; H, 7.62; N, 13.52. ESI-MS 209.12 (M+1).

2.6.6. 5-Methoxy-1,4-dimethyl-1,2,3,4-tetrahydro-quinoxaline-5,8-diol

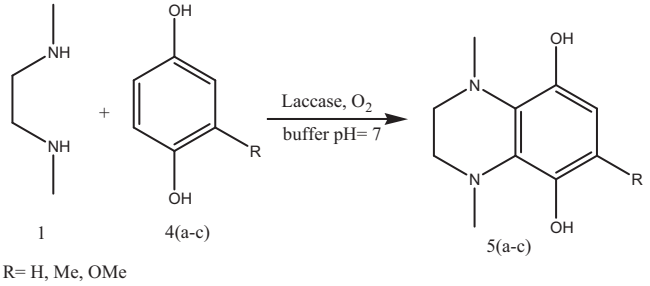
Isolated yield: 57% M.pt; mp 162–163 °C. IR(KBr) (νmax/cm^{-1}): 3420, 3418, 2929, 1587, 1528, 1475, 1411, 1359, 1313, 1284, 1196, 823, 763. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.79(s, 1H, quinone), 3.61(s, 3H, OCH_3), 3.51 (m, 4H, CH_2), 3.39(s, 3H, CH_3), 3.12(s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.2, 44.5, 45.9, 48.0, 49.4, 96.1, 109.4, 123.52, 125.8, 134.67, 136.6 Anal. Calcd for $C_{11}H_{16}N_2O_3$: C, 58.91; H, 7.19; N, 12.41. Found: C, 58.61; H, 7.26; N, 12.15. ESI-MS 225.12 (M+1).

3. Results and discussion

In order to identify suitable reaction conditions we first examined the laccase initiated reaction between N,N′-dimethylethylenediamine **1** and catechol **2a** in the presence of air. The enzyme employed was laccase isolated from *Ganoderma* sp. rckk-02 (Scheme 1). Desired product was formed after a required time period. A blank reaction was also carried out to evaluate the catalytic efficiency of laccase. There is no product formation even



Scheme 1. Reaction between N,N′-dimethylethylenediamine and different 1,2-dihydroxy benzene in the presence of laccase at room temperature.



Scheme 2. Reaction between N,N′-dimethylethylenediamine and different 1,4-dihydroxy benzene in the presence of laccase at room temperature.

after 24 h. To further explore the catalyst divergence same reaction was carried out with 1,4-benzoquinone in place of catechol. It was found that 1,4-benzoquinone is as reactive as catechol and gives desired product in quantitative yield (Scheme 2).

In addition, the effect of reaction temperature was studied by varying it from 5 °C to 60 °C. The optimal reaction temperature was found to be room temperature (25 °C). This could be attributed to the increase in the rate of decomposition and polymerization of the in situ generated quinones when a higher temperature was employed while the insolubility of the N,N′-dimethylethylenediamine was observed at lower temperature.

Table 1 shows the effect of different solvent systems on product yield. In DMSO, DMF and MeCN no reaction was observed due to denaturation of laccase. The reaction in aqueous buffer proceeded in higher yield using buffer tablets of NaH_2PO_4, Na_2HPO_4, and potassium phthalate (pH 7). The lower percentage yields in other solvent systems were due to a decrease in laccase activity in non-inter miscible organic and aqueous phases. Moreover, reaction was shown to exhibit higher reactivity and selectivity in aqueous medium rather than in organic solvents (Table 1).

The effect of enzyme concentration for the reaction was studied to determine the minimum amount of enzyme required for maximum formation of product. It is essential to optimize the concentration of the enzyme in the reaction mixture because it greatly influences the rate of reaction. In the present investigation it was observed that, the rate of laccase catalysed product formation increased with the increase in enzyme concentration and decreased after reaching optimal enzyme concentration. A similar trend was observed for all the derivatives. The optimal enzyme concentration was found to be 200 U and above which there was no appreciable change in yield of the product (Table 2). And hence 200 U of laccase is used as a standard concentration for further reactions.

The scope and generality of the present protocol was then further demonstrated by condensation of various substituted dihydroxy benzene with N,N′-dimethylethylenediamine using catalytic amount of laccase (Table 3).

For the mechanistic aspects of this new transformation, we propose a first oxidation of the dihydroxy benzene to the corresponding ketone and then electron deficient site reacts with diamine. Although intermediate is a 1,2-diketone but in this case, it is not reacting in a same manner as for quinoxaline synthesis via classical method [8–13]. In this case its electron deficient site is more prone attacked by amine (Scheme 3).

The oxidation of catechol (**2a**) in the presence of N,N′-dimethylethylenediamine (**1**) was studied using aqueous buffer solution of NaH_2PO_4, Na_2HPO_4 and potassium phthalate tablet of various pHs. The results show that with decrease in pH value of solvent, protonation of N,N′-dimethylethylenediamine occurs and it lead to the subsequent inactivation towards a Michael addition. On the other hand, the basic media increase the rate of coupling reaction between anion and dianion formed from deprotonation of catechol and o-benzoquinone **4a** (dimerization reaction). So because of the decrease in the rate of

Table 1
Solvent optimization for the quinoxaline derivatives.

S. no	Solvent	Yield (%)[a]
1	1 M acetate buffer PH 4	26
2	Water	25
3	THF	30
4	Ethanol	34
5	1 M phosphate/citrate buffer pH 4.5	45
6	M phosphate/citrate buffer solution pH 7	61
7	DMSO	–
8	MeCN	–
9	DMF	–
10	Methanol	30
11	1,4-Dioxane	18

[a] Isolated yield.

Table 2
Optimization of enzyme concentration for the synthesis of quinoxaline derivatives.

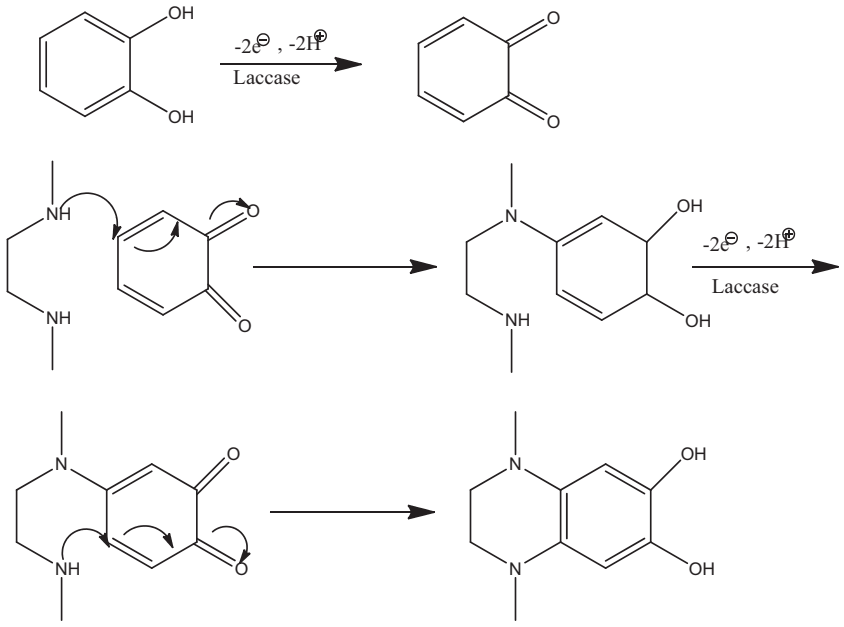
S. no	Concentration of enzyme	Yield (%)[a]
1	100 U	21
2	150 U	45
3	200 U	61
4	250 U	62

[a] Isolated yield.

Table 3
Syntheisis of quinoxalines using different dihydroxy benzene and N,N′-dimethylethylenediamine in the presence of laccase at room temperature.

Entry	Reactant	R	Time (h)	Product	Yield[a] (%)
1	**2a**	H	10	**3a**	61
2	**2b**	Me	10	**3b**	65
3	**2c**	OMe	12	**3c**	60
4	**4a**	H	9	**5a**	63
5	**4b**	Me	9	**5b**	59
6	**4c**	OMe	10	**5c**	57

[a] Isolated yield.



Scheme 3. Plausible mechanism for the synthesis of quinoxaline derivatives in the presence of laccase at room temperature.

dimerization reaction and the increase in the rate of coupling reaction between N,N′-dimethylethylenediamine (**1**) and o-benzoquinone, a solution containing buffer solution of pH = 7 is selected for the enzymatic study and synthesis of these quinoxalines. We found that the reaction can best be run at room temperature after 10 h 1,4-dimethyl-1,2,3,4-tetrahydroquinoxaline-6,7-dione **3a** was isolated as the product in 61% yield.

^{1}H NMR of catechol gave multiplet for aromatic hydrogens in the region of 6.82–6.94 ppm, N,N′-dimethylethylenediamine gave a multiplet in the region of 2.50–2.56 ppm for methylene protons and singlet at around 3.30 for methyl group protons. On the other hand, our product 3 or 5 gave as such no multiplet in the aromatic region which confirmed that two of the aromatic protons are removed during coupling with N,N′-dimethylethylenediamine. Moreover ppm values for methylene and methyl proton of N,N′-dimethylethylenediamine is changed as it is coupled with the catechol ring.

In case of ^{13}C NMR, catechol gave 3 peaks for 6 carbons in the range of 120.12, 115.5 and 146.89 ppm and N,N′-dimethylethylenediamine gave two peaks in the range of 50.5 and 133.24 ppm for two type of carbons. ^{13}C NMR of product gave 5 peaks for 5 type of carbons in the range of 39.5, 57.7, 99.9, 125.9, 138.9 ppm. Furthermore, our one of the precursor (N,N′-dimethylethylenediamine) is liquid in nature and other is solid. But we are getting solid compound as a final product which also confirm that liquid precursor is consumed during laccase catalysed reaction.

4. Conclusion

In summary, we describe a new enzymatic route for the synthesis of novel series of quinoxalines. The ambient condition, use of natural source in place of oxidative reagents not only make this methodology an alternative platform to the conventional route for the same, but it also becomes significant under the umbrella of environmental greener and safe processes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcatb.2011.11.002.

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