RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2014, **4**, 63039

Natural surfactant mediated phytosynthesis and solvatochromic fluorescence of 2-aminobenzamide derivatives

Pallavi More, Amol Patil and Rajashri Salunkhe*

Received 30th August 2014
Accepted 11th November 2014

DOI: 10.1039/c4ra09514f

www.rsc.org/advances

A green synthesis and intriguing solvatochromic behaviour of 2-aminobenzamide derivatives in varying solvents has been investigated. The biomaterial in the form of an aqueous extract of mesocarp of the fruit of the *Balanites roxburghii* plant as a natural surfactant reaction medium has been employed for phytosynthesis with quantitative yield at 60 °C. The reaction proceeds effortlessly in a short reaction time with easy product formation. The fluorescence property of some synthesized compounds was studied, along with the interesting solvatochromic behaviour of 2-amino-*N*-benzylbenzamide.

Introduction

In the past few years, microbial diseases have become a serious health care problem since resistance developed against generally used drugs is an important hurdle in the effective treatment of such infections.[1] In order to eradicate this frightening health problem, the need for development of new antimicrobials is increasing.[2] The benzamide nucleus and its various derivatives have been a fundamental point as structural units in various antibacterial compounds like benzoxazoles, oxazolidinones, and oxyclozanide[3] *etc.* They exhibit momentous chemotherapeutic as well as pharmacodynamic activities.[4] Specifically 2-aminobenzamide and its derivatives are used in the blood coagulation cascade.[5] They may serve as lead candidates in the development of novel anticancer agents[6] (Fig. 1a) and also can act as bioinspired molecular electrodes (Fig. 1b) as they possess intrinsic dipole moments and thus manifest a large propensity for self-assembly.[7] The 2-aminobenzamide acts as the starting material for several important reactions like Bargellini reaction as an competent ambident nucleophile to report successful synthesis of biologically active 1,4-benzodiazepine-3,5-dione derivatives.[8]

The design and invention of functionally diverse molecules which could serve as sensitive sensors for the analytical detection of chemically and biologically dynamic structures have turned out to be an important challenge for the scientists in recent years.[9] For this purpose, the advantages of fluorescence signalling in high selectivity and sensitivity have encouraged the development of a variety of interesting practically usable fluorescence probes.[10] 2-Aminobenzamide is a neutral and stable compound used as fluorescent tag, numerously in Glycan analysis.[11] The most frequent synthetic route for construction of 2-aminobenzamide skeleton was the condensation of isatoic anhydride and amine.[12]

In the couple of past eras, due to development of Green Chemistry, it has become one of the fundamental challenges and ultimate goals for organic synthesis to perform the reaction in water and eliminate the toxic volatile organic solvents.[13] Countless efforts have been dedicated to the finding of sustainable reaction media which diminish the problem of low solubility of organic substrates in water.[14] A range of methodologies are employed for this purpose like micellar solubilization, hydrotropy, chemical modification, pH adjustment, micronization, solid dispersion, complexation, co-solvency *etc.*[15] Out of which we preferred micellar solubilization by using surfactant for our study; as it is simple, rapid, and non-expensive and also organic transformations can be carried out in aqueous medium. The use of micellar surfactant as catalyst is

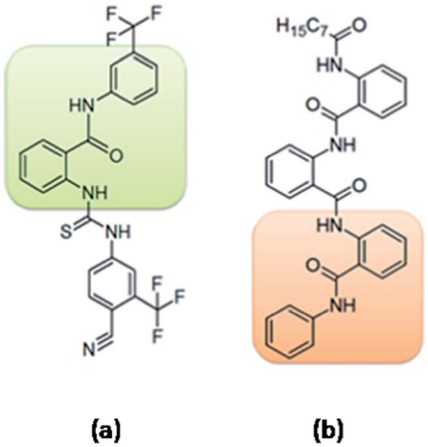


Fig. 1 2-Aminobenzamide derivatives as (a) anticancer agent; (b) bioinspired molecular electrode.

Department of Chemistry, Shivaji University, Kolhapur, 416004, M.S., India. E-mail: rsschem1@gmail.com; Fax: +91 231 2692333; Tel: +91 231 2609240

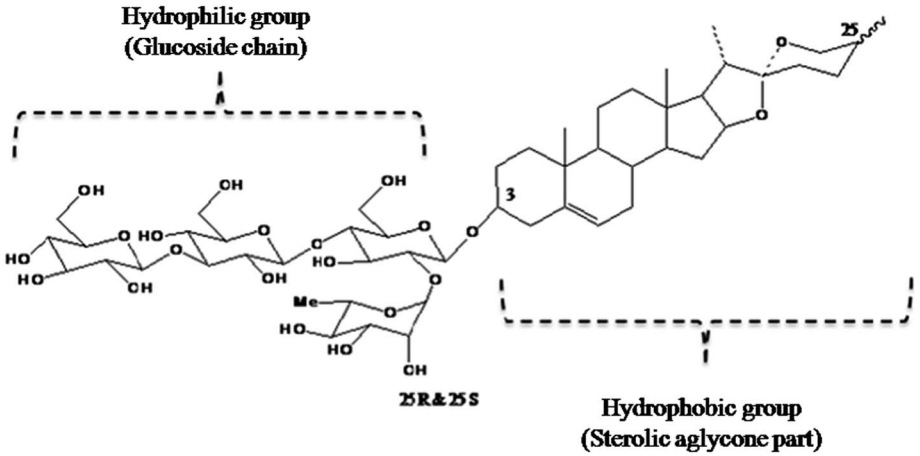


Fig. 2 Structure of Balanitiscin A.

well-known and has been explored in detail for various organic reactions.[16]

Recently, phytosynthesis *i.e.* synthesis by using plant material, have been considered as potential way for catalytic biotransformation, and it is well recognized that crude preparations of certain plants can serve as selective, high-yielding and biodegradable agents in organic synthesis.[17] In order to add contribution to the development of sustainable chemistry, we have selected a plant source, *Balanites roxburghii* as natural surfactant, which has proved to be an excellent reaction medium for organic transformation as described in our previous research work.[18] The use of surface active agents derived from natural source has a twin objective. The wide spectrum of reactions can be conducted in natural surfactants, and the use of water can lead to additional sustainability benefits which enhance the overall eco-environmental impact of the process. *Balanites roxburghii* is one of the sources of plant origin and it is recognized by several names like desert date, Hingota *etc.* and is largely dispersed in the various dry regions of India.[19,20] Balanitiscin A (Fig. 2) is one of the saponins present in the various parts of *Balanites roxburghii* plant and its structure was confirmed by D. C. Jain in the year 1987.[21] Due to chain length of the hydrophobic group (steroid part: sterolic aglycone part), the solubility of substrates is increased while the hydrophilic group (sugar part: glucoside chain) confers the buffering property and these activities are accounted as the main cause of saponin present.

Results and discussion

The preliminary efforts were made by performing a model reaction between isatoic anhydride and aniline by using 5 mL of wine red coloured aqueous extract of mesocarp of fruit of *Balanites roxburghii* plant at room temperature. Regrettably we found that the reaction was not in progress at this temperature and this can be attributed to tough elimination of carbon dioxide from isatoic anhydride. So the same reaction was studied at different temperatures and it was observed that the maximum yield was obtained at 60 °C within short reaction time (Fig. 3). Further the reaction was carried out by using 5 mL diluted aqueous extract which was almost colourless (Scheme 1) and we found that the yield of the product and pH of the catalytic solution (*ca.* 4.85) remain unaltered even after dilution. This specifies that the used natural surfactant exhibits buffering action because of which the reaction is activated in a very fast way. The acidic pH of the catalytic solution helps to enhance the rate of reaction. When the control experiment was performed, we observed that a negligible (less than 1%) yield was obtained in the absence of natural surfactant.

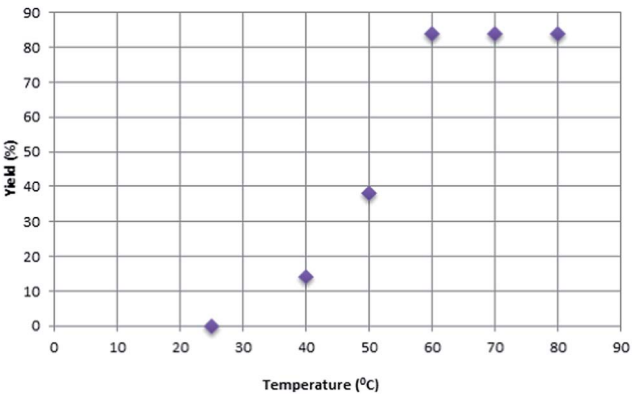
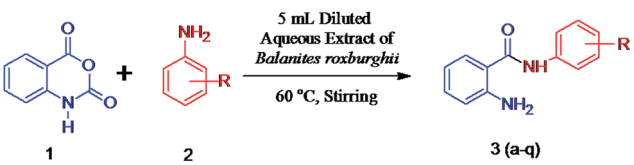


Fig. 3 Effect of temperature on reaction of isatoic anhydride (1 mmol), aniline (1 mmol) in 5 mL of diluted aqueous extract of *Balanites roxburghii* plant.



Scheme 1 Synthesis of 2-aminobenzamides in aqueous extract of mesocarp of fruit of *Balanites roxburghii* plant.

Table 1 Synthesis of 2-aminobenzamide derivatives by using aqueous extract of mesocarp of fruit of *Balanites roxburghii* plant[a,b]

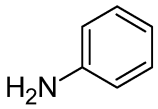
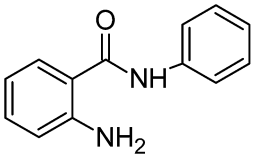
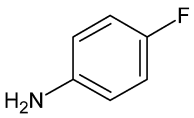
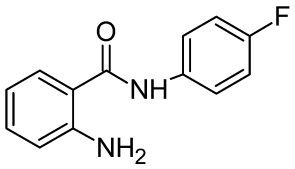
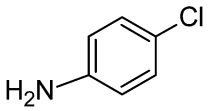
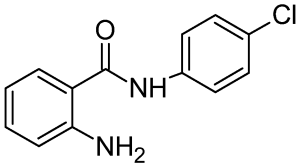
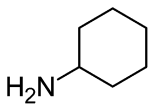
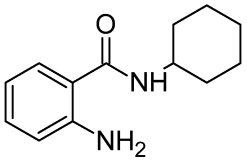
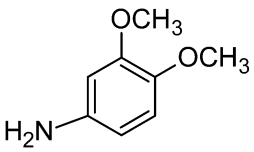
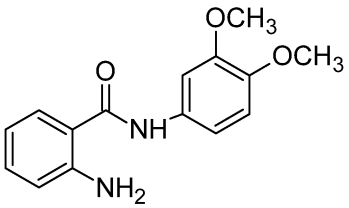
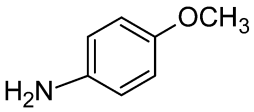
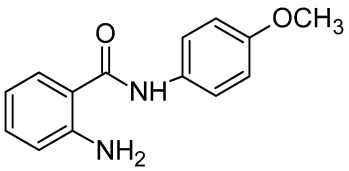
Entry	Amines	Product	Time (min)	Yield[c] (%)	M.P. (°C) [Lit.][d]
1		 **(3a)**	05	84	132 [131][3b]
2		 **(3b)**	10	86	120 [122][12a]
3		 **(3c)**	10	87	144 [147][5]
4		 **(3d)**	15	88	148 [153][3b]
5		 **(3e)**	20	85	160 [166][12a]
6		 **(3f)**	10	90	120 [121][12a]

Table 1 (*Contd.*)

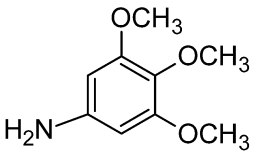
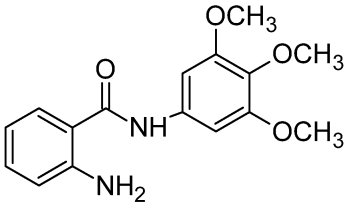
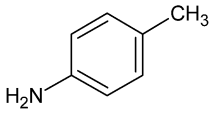
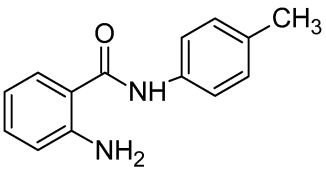
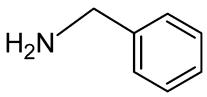
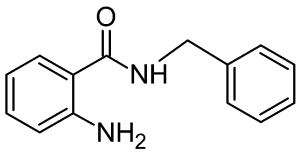
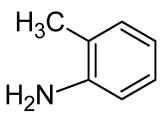
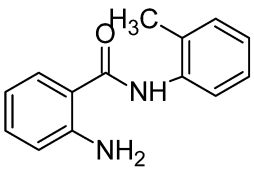
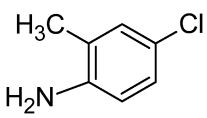
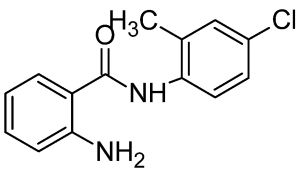
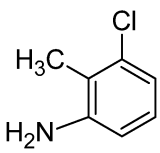
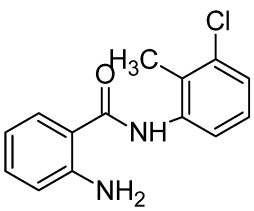
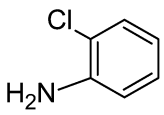
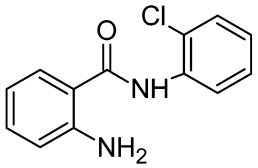
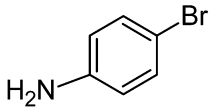
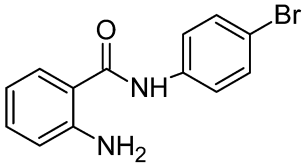
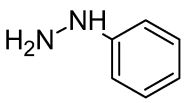
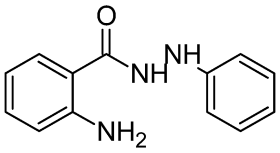
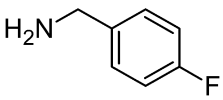
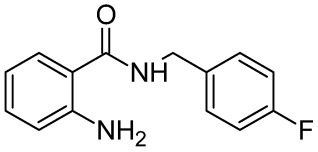
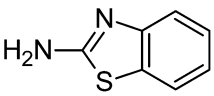
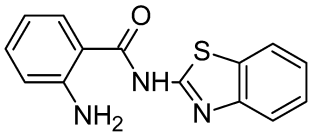
Entry	Amines	Product	Time (min)	Yield[c] (%)	M.P. (°C) [Lit.][d]
7		 **(3g)**	20	85	210 [217][12a]
8		 **(3h)**	15	86	142 [149][12a]
9		 **(3i)**	20	85	120 [122][12c]
10		 **(3j)**	20	83	102 [105][3b]
11		 **(3k)**	30	84	130 [136][3b]
12		 **(3l)**	20	86	122 [126][3b]

Table 1 (*Contd.*)

Entry	Amines	Product	Time (min)	Yield[c] (%)	M.P. (°C) [Lit.][d]
13		 **(3m)**	10	82	102 [104][3b]
14		 **(3n)**	20	84	150 [155][3b]
15		 **(3o)**	30	76	171
16		 **(3p)**	25	86	122
17		 **(3q)**	35	75	170

[a] Reaction conditions: isatoic anhydride (1 mmol), amine (1 mmol) in 5 mL of diluted aqueous extract of *Balanites roxburghii* plant at 60 °C. [b] Some representative products were characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analyses. [c] Isolated yields. [d] Literature values in parentheses.

With an eye toward the synthesis of a series of 2-aminobenzamide derivatives, various structurally diverse amines were reacted with isatoic anhydride in 5 mL of diluted aqueous extract of *Balanites roxburghii* plant at 60 °C to yield the desired products and the outcomes are enlisted in Table 1. The results revealed that the amines with electron donating groups are helpful for the reaction giving good yields. Some representative products were characterized by IR, ^{1}H NMR, ^{13}C NMR and elemental analyses. The appearance of distinct peak at 1610–1640 cm^{-1} in the IR spectra reveals the presence of amide carbonyl functional group which confirms the formation of corresponding product. The natural surfactant can be reused for number of subsequent reactions with the identical starting materials without significant change in the yield of the products.

The reaction is initiated after formation of micelles which act as microreactors.[22] Formation of micelle is indicated by turbid emulsion on stirring the reaction mixture for few

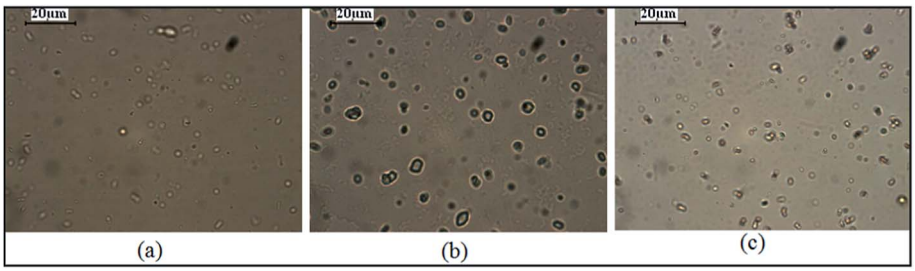


Fig. 4 Optical micrograph of the reaction mixture of aniline with isatoic anhydride in the presence of natural surfactant; (a) at the start of the reaction; (b) in the middle of the reaction; (c) at the end of reaction.

minutes. Optical micrograph of the reaction mixture after formation of turbidity (Fig. 4) is used to confirm the formation of spherical droplets (microbubbles) in water. This clarifies that isatoic anhydride and amine, both being hydrophobic, are forced within the hydrophobic core of micelle due to which reaction is promoted appreciably in forward direction.

With a series of 2-aminobenzamides in hand, our next challenging task was to prove the applicability of synthesized compounds. Some of the derivatives showed very interesting fluorescence properties. The absorption and emission maxima measured in ethyl alcohol were significantly red shifted. Preliminary absorption properties of compound **3i** were investigated by UV-Vis spectroscopy. In ethyl alcohol solution, it showed an absorption band (λ_{max}) at 326 nm (Fig. 5A). Absorption spectra of **3i** were recorded in solvents of varying polarity and were similar in appearance with no significant changes. While the compound exhibited an intense peak in its fluorescence absorption spectrum at 374 nm (λ_{ex}). The compound **3i** showed an intense peak in its fluorescence emission spectrum at 415 nm (λ_{em}) (Fig. 5B). Similarly the fluorescence behaviour of compounds **3o** (Fig. 5C), **3p** (Fig. 5D), and **3q** (Fig. 5E) were investigated by measuring their fluorescence emission spectra.

In order to address applicability of **3i** as fluorescent sensor, the effect of solvent polarity on its fluorescence spectrum was studied. Remarkably, from the data obtained (Fig. 6) we claim that the fluorescence maxima (λ_{em}) of **3i** showed red shift due to increase in solvent polarity.

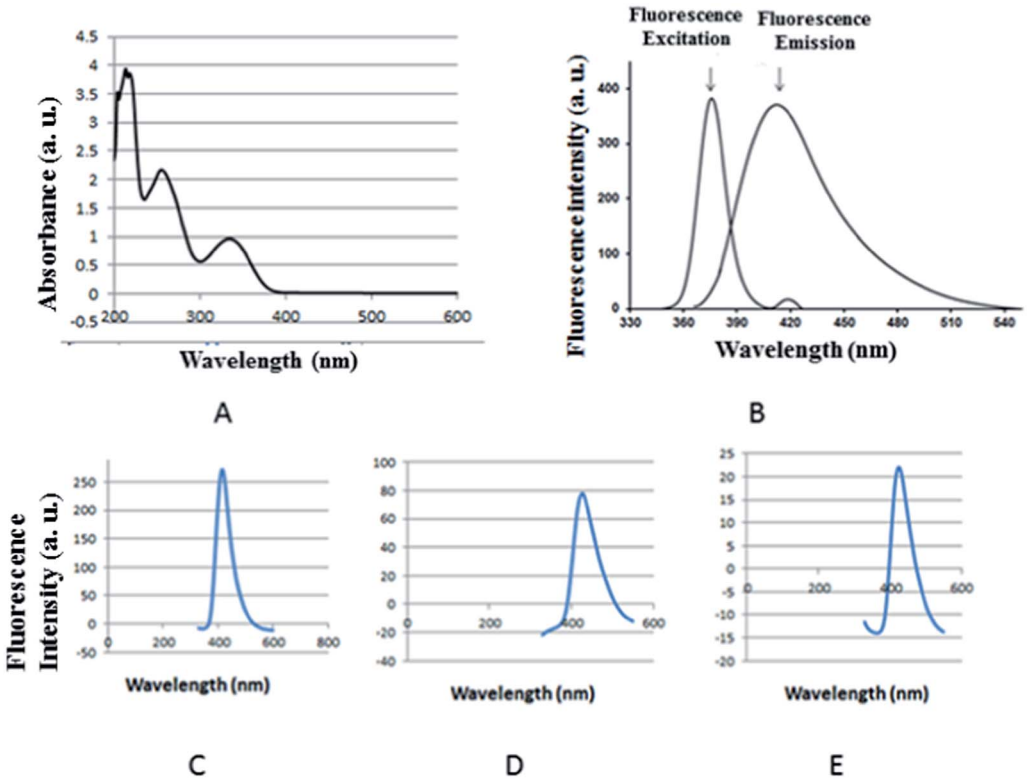


Fig. 5 (A) UV absorption spectrum of 2-amino-*N*-benzylbenzamide; (B) fluorescence excitation and emission spectra of 2-amino-*N*-benzylbenzamide; (C), (D) and (E) emission spectra of 2-amino-*N*′-phenylbenzohydrazide; 2-amino-*N*-(4-fluorobenzyl)benzamide; and 2-amino-*N*-(1,3-benzothiazol-2-yl)benzamide respectively.

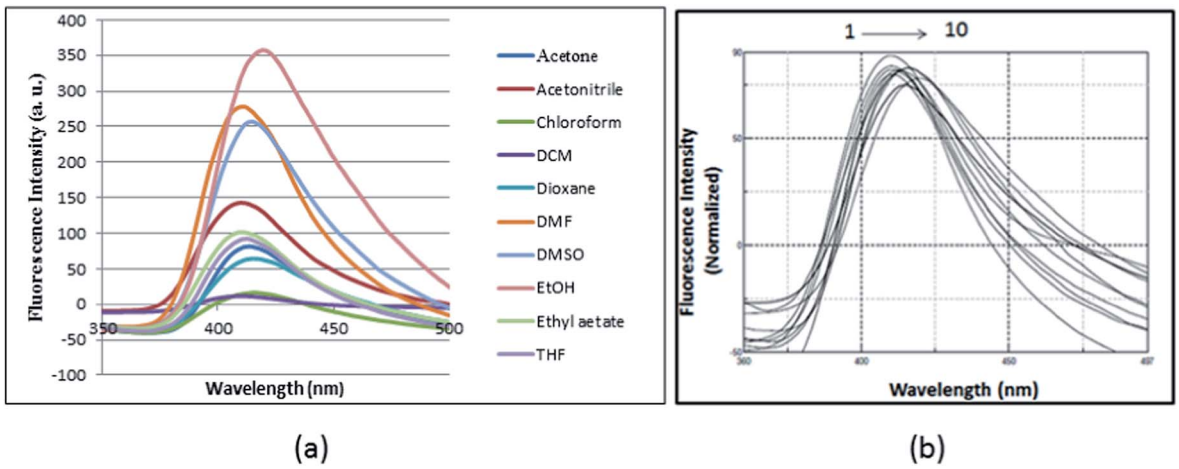


Fig. 6 (a) Solvatochromic study of compound **3i**; (b) normalized fluorescence spectra of compound **3i** in various solvents. Solvents: from left to right, 1, DCM; 2, DMF; 3, acetonitrile; 4, THF; 5, chloroform; 6, acetone; 7, ethyl acetate; 8, dioxane; 9, DMSO; and 10, ethanol.

Conclusion

In conclusion, we have developed a new, highly competent phytosynthesis for 2-aminobenzamides in which the green source *i.e.* aqueous extract of mesocarp of fruit of *Balanites roxburghii* plant is explored. The results presented in this work demonstrated a triple E (Eco-Environment and Efficient) method which offers several advantages including mild reaction conditions, enhanced reaction rates, clean reaction profiles, small quantity of biodegradable catalyst, operational and experimental simplicity. Thus the surfactant based on either a natural polar head group or hydrophobic tail group has bright future in organic transformations. This is very attractive method from both an economical and environmental point of view. Some of the synthesized compounds showed intriguing fluorescence property along with the solvatochromic behaviour, which indicate that these compounds can prove to be useful as fluorescent markers in biological systems.

Experimental

Materials

All commercial reagents were used as received without purification. The reaction was monitored by thin layer chromatography using 0.25 mm Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light. Melting points were recorded in open capillaries. The ^{1}H NMR and ^{13}C NMR were recorded on Bruker Avon spectrometer at 300 and 75 MHz respectively. Chemical shifts are reported in ppm downfield from TMS as an internal standard; coupling constants J are given in Hertz. The fluorescence spectra were recorded on PC-based spectrofluorimeter, JASCO, Japan (Model FP-750). The elemental analyses were performed on EURO EA3000 vectro model. Infrared spectra were recorded on Perkin-Elmer FT-IR spectrometer.

Methods

General procedure for the preparation of aqueous extract of mesocarp of fruit of *Balanites roxburghii* plant. Dried fruits of *Balanites roxburghii* plant were purchased from local market and authenticated from Department of Botany, Shivaji University, Kolhapur-416004 (India). Aqueous extract of fruits was prepared by soaking 3–4 g powder of mesocarp of fruit in 100 mL distilled water for 12 h. The material was smashed and then the resultant solution was filtered through Whatman filter paper no. 42. The wine red colored filtrate was used as the biocatalyst *i.e.* aqueous extract of mesocarp of fruit of *Balanites roxburghii* plant. It was stored below 5 °C and its activity remained unaffected for more than three months.

General procedure for the synthesis of 2-aminobenzamide derivatives. A mixture of isatoic anhydride (1 mmol), amine (1 mmol) and 5 mL of diluted aqueous extract of *Balanites roxburghii* plant was stirred at 60 °C for the appropriate time till the completion of reaction as monitored by thin layer chromatography (Pet ether : ethyl acetate, 7 : 3). The product was filtered, washed with distilled water, dried and recrystallized from ethyl alcohol.

Spectral analysis of representative compounds

2-Amino-*N*-phenylbenzamide (3a). Pale yellow solid, mp 132 °C; IR (KBr, cm^{-1}): 3439 (NH stretch), 3362, 3295 (NH_2 symm and antisymm stretch), 3054 (C–H stretch of aromatic ring), 1621 (C=O stretch of amide group), 1515, 1439, 1317 (C–N stretch), 1253, 1155; ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): δ 6.723 (2H, d, J = 7.5 Hz, HAr), 6.799 (1H, t, J = 7.5 Hz, HAr), 7.247–7.298 (2H, m, HAr), 7.412–7.526 (4H, m, HAr), 7.934–7.966 (2H, m, NH_2), 8.497 (1H, s, NH); ^{13}C NMR: δ 115.19, 118.63, 120.89, 125.95, 126.86, 130.16, 133.46, 134.43, 136.28, 152.13, 160.40; anal. for $C_{13}H_{12}N_2O$ (212.24) calcd; C, 73.56; H, 5.70; N, 13.20. Found: C, 73.54; H, 5.71; N, 13.21%.

2-Amino-*N*-(4-methoxyphenyl)benzamide (3f). White solid; mp 120 °C; IR (KBr, cm^{-1}): 3443 (NH stretch), 3337, 3281 (NH_2 symm and antisymm stretch), 3011 (C–H stretch of aromatic

ring), 1627 (C=O stretch of amide group), 1533, 1481, 1333 (C–N stretch), 1211; ^{1}H-NMR (300 MHz, $CDCl_3$) (ppm): δ 3.811 (3H, s, OCH_3), 5.872 (2H, s, NH_2), 6.763–6.781 (2H, m, HAr), 7.038–7.056 (2H, m, HAr), 7.223 (1H, d, $J = 7.5$ Hz, HAr), 7.371 (2H, d, $J = 7.8$ Hz, HAr), 7.443–7.489 (3H, m, HAr), 7.684 (1H, s, NH); ^{13}C-NMR: δ 56.13, 116.33, 117.01, 117.86, 122.12, 127.64, 132.16, 133.59, 137.61, 151.23, 169.28; anal. for $C_{14}H_{14}N_2O_2$ (242.11) calcd; C, 69.41; H, 5.82; N, 11.56; O, 13.21. Found: C, 70.11; H, 5.57; N, 11.62; O, 12.70%.

2-Amino-*N*-(*p*-tolyl)benzamide (3h). Pale yellow solid; mp 142 °C; IR (KBr, cm^{-1}): 3450 (NH stretch), 3321, 3249 (NH_2 symm and antisymm stretch), 2981 (C–H stretch of aromatic ring), 1628 (C=O stretch of amide group), 1549, 1440, 1316 (C–N stretch), 1198; ^{1}H-NMR (300 MHz, $CDCl_3$) (ppm): δ 2.281 (3H, s, CH_3), 5.637 (2H, s, NH_2), 6.871–6.890 (2H, m, HAr), 7.218 (2H, d, $J = 7.5$ Hz, HAr); 7.385 (1H, d, $J = 7.2$ Hz, HAr), 7.437–7.481 (3H, m, HAr), 7.882 (1H, s, NH); ^{13}C-NMR: δ 20.77, 115.22, 116.33, 117.34, 121.97, 128.41, 132.65, 133.91, 136.53, 150.16, 167.44; anal. for $C_{14}H_{14}N_2O$ (226.11) calcd; C, 74.31; H, 6.24; N, 12.38; O, 7.07. Found: C, 73.98; H, 6.11; N, 12.62; O, 7.29%.

2-Amino-*N*-benzylbenzamide (3i). Cream colored powder; mp 120 °C; IR (KBr, cm^{-1}): 3472 (NH stretch), 3359, 3304 (NH_2 symm and antisymm stretch), 3054 (C–H stretch of aromatic ring), 1630 (C=O stretch of amide group), 1578, 1541, 1444, 1414, 1324 (C–N stretch), 1269, 1150, 1026; ^{1}H-NMR (300 MHz, $CDCl_3$) (ppm): δ 4.628 (2H, d, $J = 5.4$ Hz, CH_2), 5.569 (2H, br s, NH_2), 6.352 (1H, br s, NH), 6.624–6.720 (2H, m, HAr), 7.197–7.383 (7H, m, HAr); ^{13}C-NMR: δ 43.75, 116.58, 117.34, 127.05, 127.54, 127.79, 128.77, 132.37, 138.46, 149.19, 169.34; anal. for $C_{14}H_{14}N_2O$ (226.27) calcd; C, 74.31; H, 6.24; N, 12.38. Found: 74.30; H, 6.25; N, 12.36%.

2-Amino-*N*′-phenylbenzohydrazide (3o). Cream colored powder; mp 171 °C; IR (KBr, cm^{-1}): 3429 (NH stretch), 3335, 3243 (NH_2 symm and antisymm stretch), 3021 (C–H stretch of aromatic ring), 1613 (C=O stretch of amide group), 1587, 1443, 1310 (C–N stretch), 1241, 1155, 1086; ^{1}H-NMR (300 MHz, $CDCl_3$) (ppm): δ 5.537 (2H, br s, NH_2), 6.298 (1H, br s, NH), 6.716 (2H, t, $J = 7.2$ Hz, HAr), 6.945 (3H, t, $J = 7.2$ Hz, HAr), 7.248–7.313 (4H, m, HAr), 7.489–7.517 (1H, d, $J = 7.2$ Hz, HAr), 7.777 (1H, br s, NH); ^{13}C-NMR: δ 113.19, 113.68, 116.69, 117.46, 121.36, 126.97, 129.25, 133.21, 148.27, 149.26, 169.50; anal. for $C_{13}H_{13}N_3O$ (227.26) calcd; C, 68.70; H, 5.77; N, 18.49. Found: C, 68.73; H, 5.74; N, 18.50%.

2-Amino-*N*-(4-fluorobenzyl)benzamide (3p). Pale yellow solid; mp 122 °C; IR (KBr, cm^{-1}): 3474 (NH stretch), 3357, 3315 (NH_2 symm and antisymm stretch), 3049 (C–H stretch of aromatic ring), 1629 (C=O stretch of amide group), 1538, 1303 (C–N stretch), 1219, 1159; ^{1}H-NMR (300 MHz, $CDCl_3$) (ppm): δ 4.589 (2H, d, $J = 7.5$ Hz, CH_2), 6.383 (1H, br s, NH), 6.631–6.743 (2H, m, HAr), 7.023–7.080 (2H, m, NH_2), 7.209–7.359 (6H, m, HAr); ^{13}C-NMR: δ 43.01, 115.47, 115.66, 115.75, 116.65, 117.42, 127.05, 129.39, 129.49, 132.51, 134.11, 148.86, 160.60, 163.86, 169.20; anal. for $C_{14}H_{13}N_2FO$ (244.26) calcd; C, 68.84; H, 5.36; F, 7.78; N, 11.47. Found: C, 68.80; H, 5.38; F, 7.80; N, 11.50%.

2-Amino-*N*-(1,3-benzothiazol-2-yl)benzamide (3q). White solid; mp 166 °C; IR (KBr, cm^{-1}): 3730 (NH stretch), 3444, 3419 (NH_2 symm and antisymm stretch), 3054, 2917 (C–H stretch of aromatic ring), 2500, 2340, 1658 (C=O stretch of amide group), 1558, 1451, 1309 (C–N stretch), 1246, 1161; ^{1}H-NMR (300 MHz, $CDCl_3$) (ppm): δ 6.691–6.783 (4H, m, HAr), 7.310–7.401 (3H, m, HAr), 7.487–7.538 (1H, m, NH), 7.859 (1H, t, $J = 8.1$ Hz), 7.957–8.019 (2H, m, NH_2); ^{13}C-NMR: δ 116.43, 116.74, 121.42, 124.06, 128.50, 132.12, 134.86, 151.06; anal. For $C_{14}H_{11}N_3SO$ (269.32) calcd; C, 62.43; H, 4.12; N, 15.60; O, 5.94, S, 11.91. Found: C, 62.40; H, 4.10; N, 15.64; O, 5.96; S, 11.90%.

Acknowledgements

We gratefully acknowledge the financial support from the Department of Science Technology and University Grants Commission for FIST and SAP respectively. One of the authors Pallavi More thanks the Department of Science Technology, New Delhi, India for the award of PURSE fellowship. We also express our thanks to Prof. Dr S. R. Patil, Department of Chemistry, Shivaji University, Kolhapur for useful discussion regarding the fluorescence spectroscopic studies.

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