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Solvent Free Green Synthesis of 4-substituted thiocarbamido-naphthols

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ABSTRACT

Recently in this laboratory we developed new solvent free green synthetic methods for the synthesis of 4-phenylthiocarbamido-1-naphthol, 4-(*p*-chloro)phenylthiocarbamido-1-naphthol, 4-(*o*-methyl)phenylthiocarbamido-1-naphthol, 4-(*p*-methyl)phenylthiocarbamido-1-naphthol, and 4-(*m*-methyl)phenylthiocarbamido-1-naphthol by interacting 4-amino-1-naphthol with *p*-chlorophenylisothiocynate, *p*-tolylisothiocynate, *o*-tolylisothiocynate and *m*-tolylisothiocynate in presence of sweet lemon juice, lemon and orange juice respectively which are hither to unknown. Yet such attempts were not carried out by any researcher for 4-amino-1-naphthol. Previous researchers carried out such type of synthesis for different molecules in organic solvents as medium, which are hazardous and make pollution of environment. Newly synthesized substituted thiocarbamidonapthols was characterized by elemental analysis, chemical characteristics and spectral studies.

Keywords: Green synthesis, 4-substituted thiocarbamido naphthols

INTRODUCTION

The literature survey reveals that several modern theories and concept concerning to the physical as well as chemical study of benzenoid, nonbenzenoid, heterocycles and heterocycles these compounds have their own individuality[1-5]. These compounds showed remarkable medicinal, biochemical, industrial, agricultural and pharmaceutical sciences. Thiocarbamido nucleus showed antimicrobial property as well as it acts as a versatile reagent in organic synthesis. Now-a-days thiocarbamido nucleus containg molecules showed great significances and scientific interest due their biological reactivity and biological features[6-13]. Various derivatives of this group have useful applications, some of these showed anti-tuberculosis, anti-tumor, anti-cancer, and anti-pyretic activities[14-22]. Considering all these things present research work is carried out solvent free green

synthesis to synthesized new series of substituted thiocarbamido naphthols by the interaction of 4-amino-1-naphthol with phenylisothiocynate, *p*-chlorophenyl isothiocynate, *p*-tolylisothiocynate, *o*-tolylisothiocynate and *m*-tolylisothiocynate in presence of lemon juice, sweet lemon juice and orange juice respectively which are hither to unknown. Scheme of synthesis is given in Figure 1.

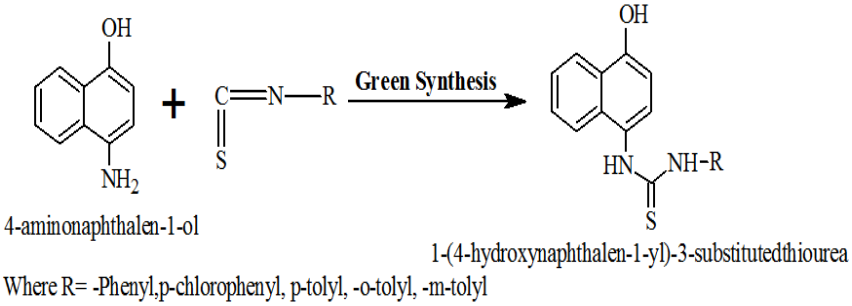


Fig. 1. (Synthesis of Substituted Thiocarbamido Naphthols)

EXPERIMENTAL

Glassware: All glassware used throughout the research work is of Borosil make.

Chemicals: India make all chemicals were used of AR grade of Merck and Aldrich. Perkin-Elmer spectrum RXI FTIR was used for IR Spectra and Bruker DRX-300 spectrometer operating at 300 MHz was used for ^{1}H NMR spectra and solvent used $CDCl_3$. Characterization was done at SAIF, Chandigarh, Punjab.

RESULT AND DISCUSSION

4-(p-Methyl)phenylthiocarbamido-1-naphthol

Solvent free interaction of 4-amino -1-naphthol (0.1 M) and *p*-tolylisothiocynate (0.1 M) was carried out in sun light in presence of lemon juice (15 mL) which gave ivory colour needle shaped crystalline product. It was recrystallized by ethanol. Yield is 92.00% and melting point is 187-188°C. Same interactions were carried out in sweet lemon juice as well as orange juice to check the percentage of yields and purity.

Properties: Compound is ivory colour crystalline solid. Compound having melting point 187-188°C. Test for nitrogen and sulphur was positive. Presence of C=S group conform on the basis of positive alkaline plumbite test. Product was soluble in acetone, ethanol, benzene, dioxane, DMSO, $DMSOd_6$ and water insoluble. IR spectrum (cm^{-1}): KBr pallets was used for IR spectrum of compound. The essential absorptions are correlated as: N-H stretching at 3295.52 cm^{-1}, Phenolic-OH stretching at 1282.82 cm^{-1}, Aromatic C-H stretching at 3059.54 cm^{-1}, Aliphatic C-H stretching at 2969.54 cm^{-1}, N-C-N stretching at 1605.81 cm^{-1}, C-N stretching at 1520.94 cm^{-1}, C-C stretching at 1390.74 cm^{-1}, C-O stretching at 1282.72 cm^{-1}, N-C=S stretching at 1520.94 cm^{-1}, C=S stretching at 912.37 cm^{-1}. PMR spectrum: DMSO was used for the PMR spectrum of a compound. Due to presence of naphthol ring this spectrum distinctly displayed the signals six protons at δ 8.2072-7.0867 ppm, Ar-H protons at δ 6.9071- 6.6549 ppm, phenolic –OH proton at δ 5.4632-5.2534 ppm, NH protons at δ 3.3706 ppm, and CH_3 protons at 1.4823-1.2406.

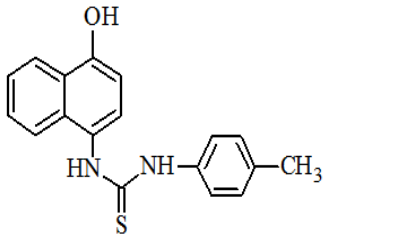


Fig. 2. 4-(*p*-Methyl)phenylthiocarbamido-1-naphthol

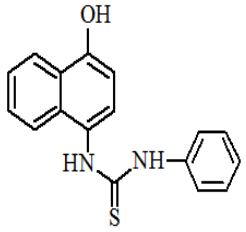
Synthesis of 4-phenylthiocarbamido-1-naphthol

Solvent free interaction of 4-amino-1-naphthol (0.1 M) and phenylisothiocynate (0.1 M) was carried out in lemon juice (15 mL) in presence of sun light which gave yellow colour needle shaped crystalline product. It was recrystallized by ethanol. Yield is 91.41% and melting point is 203-204°C. Same reactions were carried out in sweet lemon juice as well as orange juice to check the percentage of yields and purity.

Properties: Compound is yellow needle

shaped crystalline solid. It having melting point 203-204°C. Test for nitrogen and sulphur was positive. Presence of C=S group conform on the basis of positive alkaline plumbite test. Product was soluble in acetone, ethanol, benzene, dioxane, DMSO, $DMSOd_6$ and water insoluble. IR spectrum (cm^{-1}): KBr pallets was used for IR spectrum of compound. The essential absorptions are correlated as: N-H stretching at 3171.11 cm^{-1}, phenolic–OH stretching at 1598.09 cm^{-1}, aromatic C-H stretching at 2971.47 cm^{-1}, aliphatic C-H stretching at 2745.79 cm^{-1}, N-C-N stretching at 1598.09 cm^{-1}, C-N stretching at 1368.88 cm^{-1}, C-C stretching at 1598.09 cm^{-1}, C-O stretching at 1275.97 cm^{-1}, N-C=S stretching at 1275.97 cm^{-1}, C=S stretching at 1159.27 cm^{-1}. PMR spectrum: DMSO was used for the PMR spectrum of a compound. This spectrum distinctly displayed the signals due to Ar-H protons at δ 6.9071-6.6549 ppm, naphthol ring six protons at δ 8.2072-7.0867 ppm, phenolic –OH proton at δ 5.4632-5.2534 ppm, NH protons at δ 3.3706 ppm, and CH_3 protons at 1.2406.

The compound was assigned the structure as 4-phenylthiocarbamido-1-naphthol, from the above chemical characteristics, elemental and spectral analysis.



1-(4-hydroxynaphthalen-1-yl)-3-phenylthiourea

Fig. 3. 4-phenylthiocarbamido-1-napthol

Similarly, solvent free interactions of 4-amino-1-naphthol with *p*-chlorophenyl-isothiocynate, *p*-tolylisothiocynate, *o*-tolylisothiocynate and *m*-tolylisothiocynate in presence of sweet lemon juice, sweet lemon juice and orange juice were carried out in sun light respectively and results are listed in following.

TABLE 1:

Sr. No	4-Substituted thiocarbamido-1-naphthol	Melting Point (°C)	Yield in lemon Juice (%)	Yield in Sweet lemon Juice (%)	Yield in orange Juice (%)
1	4-(p-Methyl)phenyl--	187-188	92.00	---------	---------
2	4-(p-Methyl)phenyl--	187-188	---------	91.50	---------
3	4-(p-Methyl)phenyl--	187-188	---------	---------	91.50
4	4-Phenyl--------	203-204	91.41	----------	---------
5	4-Phenyl--------	203-204	----------	90.20	----------
6	4-Phenyl--------	203-204	----------	----------	89.90
7	4-(p-Chloro)phenyl--	217-218	90.00	----------	---------
8	4-(p-Chloro)phenyl--	217-218	----------	87.53	----------
9	4-(p-Chloro)phenyl--	217-218	----------	----------	87.00
10	4-(o-Methyl)phenyl--	167-168	92.68	----------	---------
11	4-(o-Methyl)phenyl--	167-168	----------	90.00	----------
12	4-(o-Methyl)phenyl--	167-168	----------	----------	90.00
13	4-(m-Methyl)phenyl-	175-176	91.50	----------	---------
14	4-(m-Methyl)phenyl-	175-176	----------	89.88	----------
15	4-(m-Methyl)phenyl-	175-176	----------	----------	89.80

CONCLUSION

It is observed from the literature survey, in our research group different type of thiocarbamide were synthesized by using acetone[23-24] and acetone-ethanol (1:1) medium. It is also observed from the literature survey 5-thiocarbamide naphthol were synthesized in acetone medium[25], but green synthetic methods are not investigated yet. The beauty of this research work and article said that in our synthetic method green synthesis parameter were maintain. It means that we didn't use any type hazardous organic solvent as medium as well as we don't use artificial heating condition means in our synthesis acetone-ethanol medium are not used and refluxion of the reaction mixture steps is also removed. Means all these reaction as well as synthesis as eco-friendly and protect the environment. It is again observed from the literature survey that the particular product yield are increase also purity of product was maintained. These molecules often have interesting biological activities.

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Conflicts of Interest

The publication of this research article authors declare that have no conflict of interest.

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