

Colorimetric Determination of Thiol Substituted Heterocyclic Compounds

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Summary: A coloured reaction occurs by the interaction between the electron acceptor, 2,6-dichloroquinone-4-chlorimide and an electron donor thiol substituted heterocyclic compound. This reaction was applied to the determination of thiols by measuring the absorbance of the reaction product which was stable upto 30 minutes. The relative standard deviation for the method was found to be ± 0.023 .

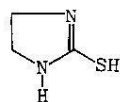
Introduction

Several reagents have been used for the assay of thiols by various methods (1-3). A spectrophotometric method was reported for the quantitative determination of thiol substituted heterocyclic compounds with chloranil [4]. The reagent 2,6-dichloroquinone-4-chlorimide was used for the spectrophotometric determination of dinitrophenyl ether and other reactants [5]. The aim of the present investigation was to examine the effect of 2,6-dichloro-quinone-4-chlorimide in the formation of stable coloured solution with thiols. Thiols were then determined by measuring the absorbance of their reaction products. Thus a new, simple and specific method for the quantitative determination of thiol substituted heterocyclic compounds with the reagent has been developed.

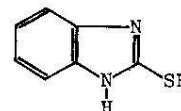
Experimental

Material (Chemicals)

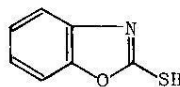
The following pure compounds were used in this study: 2-thiol-imidazoline; 2-thiol-benzimidazole; 2-thiol-benzoxazole; 2-thiol-benzthiazole; 2-thiol-thiazoline; 2,4-dichloroqui-



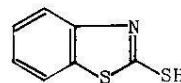
2-thiol-imidazoline



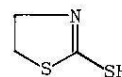
2-thiol-benzimidazole



2-thiol-benzoxazole



2-thiol-benzthiazole



2-thiol-thiazoline

none-4-chlorimide (Reagent). The purity of these compounds were checked by mixed m.p. and TLC analysis.

Solutions

- 1) Reagent solution (10^{-3} M) was freshly prepared in each experiment in 50 ml isopropanol (AR Grade, Merck).
- 2) 10^{-5} M Thiol substituted compound was prepared by dissolving it in 50 ml isopropanol.

Conditions for the Preparation of Coloured Solutions:

Coloured solution of thiol substituted heterocyclic compounds with the reagent were prepared by mixing molar solutions of both components as shown in Table-1.

Table 1: Condition for the formation of coloured product of thiol substituted heterocyclic compound with 2,6-dichloro-quinone-4-chlorimide.

Substance	Concentration of the substance 10^{-5} M	Excess of reagent, M
2-thiol-imidazoline	6.4	117
2-thiol-benzimidazole	10.2	190
2-thiol-benzoxazole	9.3	220
2-thiol-benzthiazole	9.6	133
2-thiol-thiazoline	6.7	190

Method of Analysis:

Separate solutions (3-8 ml) of each thiol compound were pipetted out into 10 ml volumetric flasks and 2.0 ml of freshly prepared reagent solution was added to each flask.

The solutions were shaken well and kept for 3-6 hours at room temperature to develop a stable colour and then the volume was made up with isopropanol. Absorbance of each solution was measured at 440 nm and 490 nm in 1 cm cuvette on a ZEISS spectrophotometer using the reagent solution as a reference. Calibration curves were prepared individually for each substituted thiol to determine its concentration.

Results and Discussion

A spectrophotometric method has been developed for the quantitative determination of thiol substituted heterocyclic compounds with 2,6-dichloroquinone-4-chlorimide as a reagent. This reagent being a strong electron acceptor has been widely used for the quantitative determi-

nation of strong electron donor indole compounds in the form of charge transfer complex (6,7). The purpose of this study was to examine the interaction of thiol substituted heterocyclic compounds with the cited reagent. It has been observed that this reagent forms coloured reaction products with thiol substituted heterocyclic compound according to a published mechanism [8]. The process of the reaction is very slow and also time consuming with thiol substituted heterocyclic compound, whereas the reagent immediately forms charge transfer complexes with heterocyclic compounds like indoles [1,2,9]. At pH 8-9 the reaction proceeds within 20-30 minutes [3]. In the absence of alkali the reaction proceeds in a few hours to its completion and the excess of reagent is needed to obtain stable coloured solution, as shown in Table-I & II.

The thiol substituted heterocyclic compounds and the reagent were mixed in a certain molar ratio in isopropanol to obtain a coloured solution as shown in Table-I. Results in Table II indicates that the stability of the coloured solution is 30 minutes, which is good enough for analytical work. The other characteristics of the coloured product and molar extinction coefficients are reported in Table-II.

Table-2 Characteristics of the Product of Thiol Substituted Heterocyclic Compound with 2,6-dichloroquinone-4-chlorimide.

Substance	Colour	Appearance of colour (minutes)	Stability of colour (minutes)	Molar extinction coefficient
1) 2-thiol-imidazoline	Orange	240	30	2340
2) 2-thiol-benzimidazole	Bright Orange	180	30	4000
3) 2-thiol-benzoxazole	Orange Yellow	300	30	2220
4) 2-thiol-benzthiazole	Yellow	190	30	2540
5) 2-thiol-thiazoline	Orange	400	30	3620

Table-3 Quantitative Determination of Thiol Substituted Heterocyclic Compounds with 2,6-dichloroquinone-4-chlorimide.

Substance	Added 10 ⁻⁵ M	Found* 10 ⁻⁵ M	S	Sr
2-thiol-imidazoline	10.23	9.96	0.150	0.015
2-thiol-benzimidazole	6.40	6.23	0.133	0.021
2-thiol-benzoxazole	7.42	7.33	0.146	0.018
2-thiol-benzthiazole	7.18	6.70	0.296	0.043
2-thiol-thiazoline	4.03	3.98	0.075	0.019

* Mean value of five readings
S=Standard deviation
S_r=Relative standard deviation

The following analytical wave lengths were used for the thiol substituted compounds, which represent the λ_{\max} of the coloured products:-

2-thiol-imidazoline, 220 nm; 2-thiol-benzoxazole, 470 nm; 2-thiol-benzimidazole, 490 nm; 2-thiol-benzthiazole, 490 nm; 2-thiol-thiazoline, 500 nm.

Results of the analysis of each thiol substituted heterocyclic compound are summarised in the Table-III. The method is simple,

reproducible and convenient for the assay of thiol. An average relative standard deviation of ± 0.023 has been achieved.

References

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