SYNTHESIS AND CHARACTERIZATION OF METHYLBENZOYLTHIOUREIDO VIA FT-IR AND UV-VIS SPECTROPHOTOMETER

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ABSTRAK

Tindak balas antara 2-, 3- dan 4-metilbenzoilisotiosianat dengan β-alanin menghasilkan asid *N*-(2-metilbenzoiltioureido)-*N'*- propanoik (I), asid *N*-(3-metilbenzoiltioureido)-*N'*- propanoik (II) and asid *N*-(4-metilbenzoiltioureido)-*N'*- propanoik (III). Kesemua sebatian ini dianalisis menggunakan Fourier Transformasi Infra-Merah (FT-IR) dan spektrofotometer Ultralembayung Cahaya Nampak (UV-Vis). Spektrum FT-IR menunjukan regangan penting, ν(N-H), ν(C=O, karboksilik), ν(C=O, amida), ν(C-N) and ν(C=S) pada 3300-3400 cm^{-1}, 1700 -1720 cm^{-1}, 1650-1680 cm^{-1}, 1300-1400 cm^{-1} dan 730-800 cm^{-1}. Terdapat dua kromofor utama, (C=O) dan (C=S) dalam sebatian ini yang boleh dilihat pada penyerapan maksimum 240nm dan 280nm.

Kata kunci: metilbenzoiltioureido, tiourea dan asid amino

Abstract

Reaction of 2-, 3- and 4-methylbenzoylisothiocyanate with β-alanine resulted *N*-(2-methylbenzoylthioureido)-*N'*-propanoic acid (I), *N*-(3-methylbenzoylthioureido)-*N'*-propanoic acid (II) and *N*-(4-methylbenzoylthioureido)-*N'*-propanoic acid (III). These compounds were characterized by FT-IR and UV-Vis spectrophotometer. The FT-IR spectrum shows the important stretching absorption band of these compounds which are ν(N-H), ν(C=O, carboxylic), ν(C=O, amide), ν(C-N) and ν(C=S) at 3300-3400 cm^{-1}, 1700 -1720 cm^{-1}, 1650-1680 cm^{-1}, 1300-1400 cm^{-1} and 730-800 cm^{-1}, respectively. Two chromophores, C=O and C=S in these compounds can be observed in UV spectra at maximum absorption at 240nm and 280nm, respectively.

Keyword: methylbenzoylthioureido, thiourea, amino acid

Introduction

Thiourea and its derivatives have been widely used in technological applications such as in the pharmaceutical industry (Dixit et.al, 2006) [1], as catalyst in chemical reactions and for extraction of toxic metals using a solid supported liquid membrane system. It is well established that thiourea derivatives compound and its complexation with transition metals has potential in anti-bacterial or anti-fungal and anti-tumor properties (Rodríguez-Fernández et.al, 2005, Li et.al, 2006) [2-3]. In addition, thiourea derivatives have been shown to possess antitubercular, antithroid, antihelmintic, insecticidal and rodenticidal properties (Xu et.al, 2003) [4]. Besides their increasing important role as intermediates in agricultural where thiourea used as herbicide to reduce the growing of parasites plant (Xue et.al, 2004) [5].

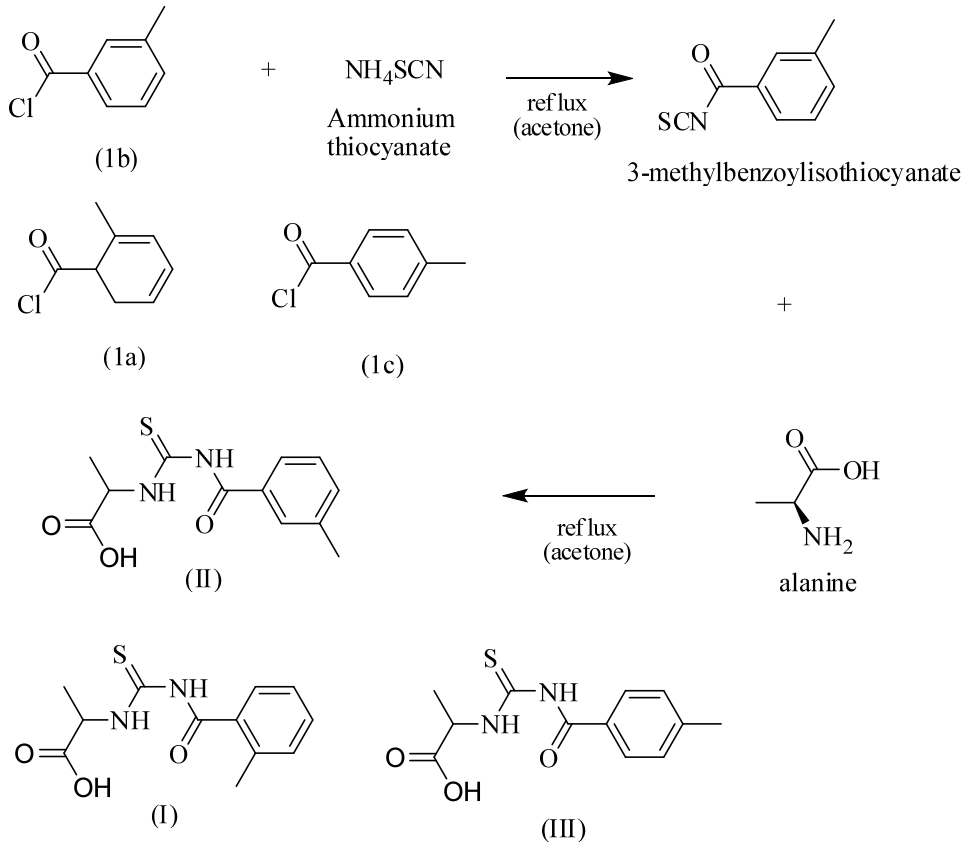
Experimental

Reagent and instrumentation

All chemicals used were reagent grade quality. FTIR spectra of methylbenzoylthioureido derivatives were recorded using KBR pellets on a Perkin Elmer Spectrometer 100 Series apparatus. Absorption spectra were recorded in cells of *quartz* 1 cm using a Shimadzu UV-vis spectrophotometer 1601 Series, all compounds are dissolved in pure methanol with the concentration 10^{-5} M.

Synthetic methodology

2-methylbenzoyl chloride (1a)/3-methylbenzoyl chloride(1b)/4-methylbenzoyl chloride(1c) (2.80 g, 20 mmol) was dissolved in 20 ml purified dry acetone and was added dropwise into a solution of ammonium thiocyanate (1.52g, 20 mmol) in 20 ml of dry acetone under reflux and stirring for 1 hour. Then, β-alanine (2.16 g, 20 mmol) was added dropwise into the reaction mixture under reflux and continuously stirring for 4 hours. Next, the mixture was poured into a beaker containing ice blocks. The precipitate was filtered and washed with cold methanol. All compound obtained were recrystallized in ethanol.



Scheme 1 Synthesis of compound I, II, and III, thiourea derivatives of amino acid

Result and Discussion

FT-IR Spectra

The characteristic *v*(N-H) stretching vibrations of methylbenzoylthioureido derivatives are appeared in the 3291-3382 cm^{-1} range. This difference between the *v*(N-H) stretching frequencies is due to intramolecular hydrogen bonding (Reetz et.al, 2000). The strong absorption of $v(C{=}O_{carboxylic})$ and $v(C{=}O_{amide})$ band in the IR spectra of the compounds are observed in the region 1700 -1720 $cm^{-1}$and 1650-1680 cm^{-1}. The C=O stretch band not sufficient evidence to identify a carboxylic acid, other band such as the O-H stretch to confirm the assignment. The C=O stretch for amide decreasing in frequencies comparing with the ordinary carbonyl absorption (1700 cm^{-1}) and C=O stretch for carboxylic.This is interpreted as being a result of its conjugated resonance and the the possible formation of intramolecular hydrogen bonding with N−H (Reetz et al, 2000). In addition, The absorption bands in the range of 1300-1400 cm^{-1} are assigned to the *v*(C−N) vibrations. The frequencies of 730-800 cm^{-1} are assigned to the *v*(C=S) vibration for compound I, II and III respectively. The lowest frequency for *v*(C=S) stretching for compound II indicated that intramolecular hydrogen bonding exists in the compound. The O-H stretch in all compounds was broad and found around 3500 cm^{-1}. The O-H stretch appeared in the spectrum resulted from amino acid.

Table 1 FTIR absorption frequencies

Compounds	*v* (cm^{-1})				
	v(N−H)	$v(C{=}O_{carboxylic})$	$v(C{=}O_{amide})$	*v*(C−N)	*v*(C=S)
I	3233.72	1705.70	1673.65	1196.19	755.92
II	3369.70	1715.79	1671.87	1392.34	798.72
III	3307.34	1719.30	1668.24	1263.34	760.81

UV spectra

There are two significant chromophores, C=O and C=S resulting from n→π* transitions have been observed in the UV spectra with maximum absorption at 240nm and 280nm, respectively. The strong absorbance peak presents a red shift in local transition and a broadening of the band with weakening of the structural vibration absorption. It is credited to the ability of methanol to protonate the oxygen atom of the C=O group or sulfur atom of the C=S group.

Conclusion

This paper reported three new menthylbenzoylthioureido derivatives and all compounds have been characterized by FTIR and UV-Vis Spectrophotometer. The C=O stretch of carboxylic acids is in the region as the other C=O stretch of ketones, aldehyde and ester.

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