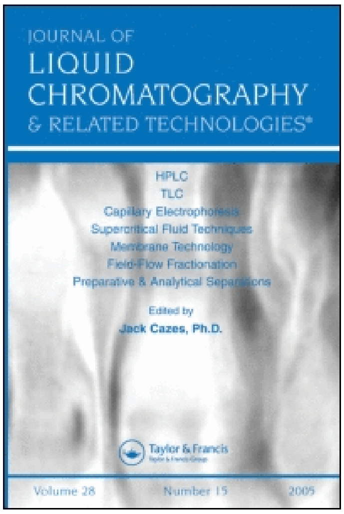

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

RP-HPLC Method for Simultaneous Determination of Thiobenzanilide and its Oxidation Products: Monitoring the Oxidation of Thiobenzanilide with Jones' Reagent

Nataša Ristovska[a]; Marina Stefova[a]; Frosa Anastasova[a]
[a] Institute of Chemistry, Faculty of Science, Skopje, Republic of Macedonia

To cite this Article Ristovska, Nataša , Stefova, Marina and Anastasova, Frosa(2005) 'RP-HPLC Method for Simultaneous Determination of Thiobenzanilide and its Oxidation Products: Monitoring the Oxidation of Thiobenzanilide with Jones' Reagent', Journal of Liquid Chromatography & Related Technologies, 28: 15, 2391 — 2401
To link to this Article: DOI: 10.1080/10826070500187574
URL: http://dx.doi.org/10.1080/10826070500187574

Journal of Liquid Chromatography & Related Technologies®, 28: 2391–2401, 2005
Copyright © Taylor & Francis, Inc.
ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070500187574

RP-HPLC Method for Simultaneous Determination of Thiobenzanilide and its Oxidation Products: Monitoring the Oxidation of Thiobenzanilide with Jones' Reagent

Nataša Ristovska, Marina Stefova, and Frosa Anastasova
Institute of Chemistry, Faculty of Science, Skopje,
Republic of Macedonia

Abstract: The reaction of thiobenzanilide with various oxidants leads to the formation of a few possible products such as benzanilide, 2-phenylbenzothiazole, thiobenzanilide-S-oxide, bis(N-phenylbenzimidoyl) disulfide, and bis(N-phenylbenzimidoyl) sulfide. The formation of these products depends on the reaction conditions and liquid chromatography is a convenient method for monitoring the oxidation reaction. In the present study, a reversed-phase HPLC method is developed for separation and simultaneous determination of thiobenzanilide and its oxidation products using an analytical column Lichrosorb RP18 (250 × 4 mm, particle diameter 5 μm) and gradient elution with acetonitrile and water with phosphoric acid (pH = 3.0). The elution is monitored in the whole UV range (diode array detector) and detection at 254 nm is chosen for all examined analytes, except for thiobenzanilide-S-oxide, for which the wavelength of 344 nm is preferred regarding sensitivity and selectivity. The calibration curves for quantitative determination of thiobenzanilide and its oxidation products were constructed in the concentration range of 2×10^{-6} mol/L-1×10^{-3} mol/L. Linear dependence of the peak area versus concentration of each analyte was established with satisfactory values of the coefficient of correlation ($R^2 > 0.99$). The proposed method was then applied for monitoring the reaction of oxidation of thiobenzanilide with Cr(VI), the so-called Jones' reagent, and the results are presented and discussed.

Keywords: Thiobenzanilide, Benzanilide, 2-Phenylbenzothiazole, Oxidation, Jones' reagent, RP-HPLC, Monitoring

Address correspondence to Nataša Ristovska, Institute of Chemistry, Faculty of Science, P.O. Box 162, 1001, Skopje, Republic of Macedonia. E-mail: natasa@iunona.pmf.ukim.edu.mk

INTRODUCTION

In the past few years, the research in our laboratory has been focused on synthesis and studies of the structural characteristics[1–4] of compounds that exhibit biological and cytostatic[5] activity. Recently, these studies were extended to thioamides and their derivatives.[6] Some previous investigations of thioamides have shown that several substituted thiobenzamides exhibit activity against M. Tuberculosis and, for this reason, they have been studied in many laboratories as potential tuberculostatic drugs.[7–9]

In order to study some chemical properties of thiobenzamides, initially their behavior on oxidation, a reversed phase HPLC method has been developed for monitoring the reaction of oxidation of these compounds. Thiobenzamides are readily attacked at the sulfur atom in the reaction of oxidation by various oxidants yielding a large variety of products: S-oxides; sulfur-free products, and heterocycles; diimidoyl disulfides and sulfides.[10–14]

Chromium oxidation, widely explored in organic chemistry, is the topic of our current interest in developing new techniques and procedures for oxidation of thiobenzamides. Cr(VI) compounds are convenient for visually following the progress of the reaction because of the dramatic color change from orange Cr^{6+} solutions to green Cr^{3+} salts. Also, chromium (VI) derivatives regarding their high oxidation potential, behave as strong oxidizing reagents capable of oxidizing almost every oxidation eligible organic functional group,[15] and giving high yields of obtained products. Still, there are no available published reports on the oxidation of the thioamide group with Cr (VI) reagent.

Our investigations on the reaction of oxidation for thiobenzanilide with Cr(VI) reagents indicate that this reaction is not a simple process, but probably involves two or more side reactions. So, the final result of the oxidation is a mixture of two or more components. Their preparative isolation is complicated and the process of re-crystallization is followed by decomposition of some thermally unstable products. In order to avoid these and similar problems, instrumental methods, of which liquid chromatography is the most convenient, can be used to determine the composition of the reaction mixture after oxidation of thiobenzanilide, and to monitor the course of the reaction.

In this paper, a reversed-phase HPLC method with UV-diode array detection is developed for separation and simultaneous determination of thiobenzanilide (**1**) and its oxidation products: thiobenzanilide-S-oxide (**2**), benzanilide (**3**), 2-phenylbenzothiazole (**4**), bis(N-phenylbenzimidoyl) sulfide (**5**), and bis(N-phenylbenzimidoyl) disulfide (**6**), and it is used for monitoring the reaction of oxidation of thiobenzanilide with Cr(VI), so called Jones' reagent, under different reaction conditions in acetone medium.

EXPERIMENTAL

Chemicals

All of the analyzed compounds were synthesized by known or modified methods. Thiobenzanilide was synthesized by thionation of benzanilide.[8] Thiobenzanilide-S-oxide was prepared by oxidation of thiobenzanilide with H_2O_2.[14] Benzanilide was prepared by addition of benzoyl chloride into aniline in 10% aqueous NaOH.[8] 2-phenylbenzothiazole was synthesized by oxidation of thiobenzanilide with potassium ferricyanide.[16] Bis(N-phenylbenzimidoyl) sulfide was obtained in high yield using thermal decomposition of organic solution from bis(N-phenylbenzimidoyl) disulfide.[11] The synthesis of bis(N-phenylbenzimidoyl) disulfide by oxidation of thiobenzanilide with lead tetraacetate was modified.[17] The standard chromium trioxide-sulfuric acid solution was prepared using the Jones' method.[15]

All crude products were purified with crystallization. The identification of the obtained compounds was performed using melting points, microanalysis, and IR spectral data.

Apparatus

The FT IR spectra were recorded with Perkin-Elmer System 2000 interferometer in the 4000-400 cm^{-1} frequency range. The spectra of all obtained crystal solids were recorded in KBr pellets. TLC analysis of the reaction mixtures and of the purified thiobenzanilide and its oxidation products were carried out on silica gel plates with benzene-ethyl acetate (9 : 1, v/v) and detection under an UV lamp, or with I_2 vapor. A Varian HPLC system equipped with ternary gradient pump Model 9012, a Rheodyne injector with 20 μL sample loop, and a UV-Diode Array detector Model 9065, was used for the HPLC analysis. Separations were performed on an analytical column LiChrospher 60 RP-select B (LiChroCART, dimensions 250 × 4 mm, 5 μm particle diameter).

Chromatographic Conditions

The proposed method was conducted using a reversed phase technique and UV monitoring. The mobile phase consisted of solvent A (water with phosphoric acid with $pH = 3.0$) and solvent B (acetonitrile, HPLC grade from Merck). The gradient elution program was: 0–10 min: 60% A; 15–25 min: 25% A. The flow rate was 1.0 mL/min. Each solution of 20 μL was injected and chromatograms were recorded. Data acquisition and management was performed using Star Workstation 4.5 software package.

Calibration Curves

A set of working standard mixture solutions was prepared by diluting aliquots of the stock solution (1×10^{-3} mol/L) with methanol to give concentrations ranging from 2×10^{-6} mol/L–1×10^{-3} mol/L for each compound studied. Each solution (20 μL) was injected into the chromatograph and chromatograms were recorded. The calibration graphs were constructed by plotting the peak areas vs. concentration of oxidation products of thiobenzanilide injected in the column and the linear relationship was evaluated by the least squares method.

Procedure

The procedure involves addition of Jones' reagent to a diluted acetone solution of thiobenzanilide in different proportions. The temperature of the reaction mixture was kept under 35°C. Chromatography of the reaction mixture was performed on a Varian HPLC system at ambient temperature.

RESULTS AND DISCUSSION

A few reversed-phase HPLC methods using various mobile phases were tested for chromatographic separations of thiobenzanilide and its oxidation products. Among these mobile phases (water acidified with acetic acid and phosphoric acid, and methanol and acetonitrile as the organic modifier), the most satisfactory resolution of thiobenzanilide and its oxidation products was achieved by a gradient elution with a mobile phase composed of aqueous phosphoric acid with $pH = 3.0$ and acetonitrile. Under the described conditions (in experimental) the elution order was the following: thiobenzanilide-S-oxide (**2**) ($t_r = 10.363$ min), benzanilide (**3**) ($t_r = 11.133$ min), thiobenzanilide (**1**) ($t_r = 15.839$ min), 2-phenylbenzothiazole (**4**) ($t_r = 17.992$ min), bis(N-phenylbenzimidoyl) sulfide (**5**) ($t_r = 21.077$ min) and bis(N-phenylbenzimidoyl) disulfide (**6**) ($t_r = 22.868$ min). The wavelength of 254 nm was selected for detection because all of the analytes exhibit significant absorption, which produces good sensitivity for all the investigated compounds, except for thiobenzanilide-S-oxide. In order to achieve a better sensitivity for this oxidation product and better resolution from benzanilide, a wavelength of 344nm was used for its determination. Namely, thiobenzanilide-S-oxide exhibits an absorption maximum and benzanilide practically does not absorb at this wavelength. A chromatogram of a standard mixture containing thiobenzanilide and its oxidation products at 254 and 344 nm is shown in Figure 1.

The values calculated for the retention factors (k), separation factors (α) and resolution (R) between adjacent peaks are given in Table 1. It can be seen that these chromatographic conditions give high efficiency of separation

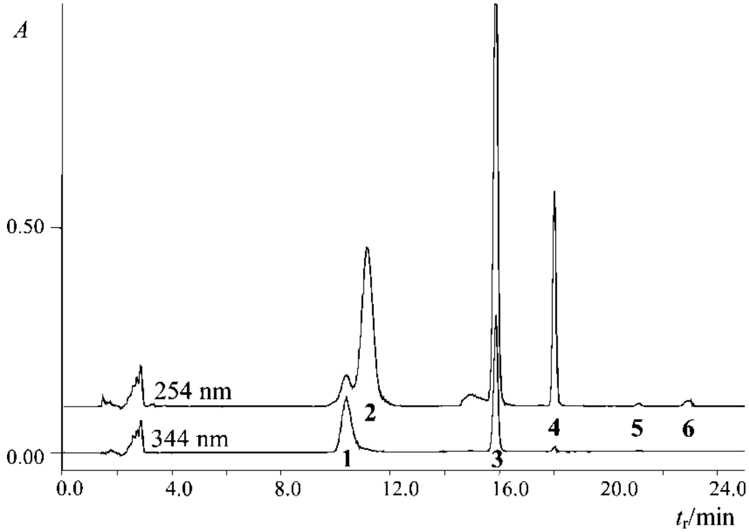

Figure 1. Chromatograms at 254 and 344 nm of a standard mixture containing: 1) thiobenzanilide-S-oxide, 2) benzanilide, 3) thiobenzanilide, 4) 2-phenylbenzothiazole, 5) bis(N-phenylbenzimidoyl)sulfide, and 6) bis(N-phenylbenzimidoyl) disulfide.

for the investigated compounds. As mentioned above, detection was performed in the whole UV-range, and quantification at 254 nm was chosen as most suitable regarding sensitivity and selectivity, except for thiobenzanilide-S-oxide. For this oxidation product, the wavelength of 344 nm was selected because of the significantly better resolution and better selectivity (α) from those on 254 nm. As can be seen in Figure 1, the peak from benzanilide does not appear in the chromatogram at 344 nm, which improves the resolution of its adjacent peaks (thiobenzanilide-S-oxide and thiobenzanilide), as shown in Table 1.

Table 1. Retention times (t_r), retention factors (k), separation factors (α) and resolution (R) for the six investigated compounds

Compound	t_r/min	k[a]	α	R
Thiobenzanilide-S-oxide 254 nm	9.928	5.284	0.936	0.758
344 nm			0.597[b]	10.406[b]
Benzanilide	10.499	5.645	0.638	9.062
Thiobenzanilide	15.570	8.854	0.859	7.808
2-Phenylbenzothiazole	17.859	10.303	0.843	11.436
Bis(N-phenylbenzimidoyl) sulfide	20.902	12.229	0.923	4.169
Bis(N-phenylbenzimidoyl) disulfide	22.509	13.246		

[a] $t_0 = 1.58$ min.

[b] Benzanilide showing no absorption at 344 nm ⇒ thiobenzanilide is the nearest peak to the peak of thiobenzanilide-S-oxide.

The linearity was calculated by the least squares method in the range from 10^{-6} to 10^{-3} mol/L for all analytes, giving a correlation coefficient $R^2 > 0.99$ for all compounds. Calibration graphs were constructed by plotting the peak area as a function of the injected amount of the analyte. The equations for the calibration curves and correlation coefficients in the working concentration range (10^{-4}–10^{-3} mol/L) are listed in Table 2.

As can be seen from Table 2, the values of the coefficient of correlation were satisfactory for all analytes, so the proposed method can be used for quantitative analysis of the oxidation products of thiobenzanilide. The higher sensitivity for thiobenzanilide-S-oxide at wavelength of 344 nm is confirmed by almost twice (1.6) higher value of the slope of the regression curve compared to the one obtained at 254 nm.

In order to establish the limits of detection and quantification of the analyzed compounds, calibration was performed in the low concentration region (10^{-6}–10^{-5} mol/L). The statistical data (standard deviation SD, correlation coefficients R^2, limit of detection LOD and limit of quantification LOQ) are given in Table 3.

The proposed reversed-phase HPLC method gives satisfactory resolution of the peaks from the possible products of oxidation of thiobenzanilide, using different oxidants and reaction conditions, and is suggested as a convenient tool for monitoring the formation of the oxidation products and studying the kinetics of these reactions. The problem that evolved by the difficulty in separating the peaks obtained for low concentration of benzanilide and thiobenzanilide-S-oxide can be resolved by using the calibration data of thiobenzanilide-S-oxide at both wavelengths (254 and 344 nm). This enables calculation of the concentration of thiobenzanilide-S-oxide at 344 nm (where the peak of the present benzanilide does not appear) and then calculation of the corresponding peak area due to the presence of thiobenzanilide-S-oxide at 254 nm. This value can then be subtracted from the total area of both, thiobenzanilide-S-oxide and benzanilide, and the result is the area due to the presence of benzanilide only. However, this

Table 2. Statistical data of calibration curves of investigated compounds in working concentrations

Compound	Regression equation	R^2
Thiobenzanilide-S-oxide 254 nm	$A = 5.590 \cdot 10^8 c - 3.093 \cdot 10^4$	0.994
344 nm	$A = 9.516 \cdot 10^8 c - 3.269 \cdot 10^4$	0.997
Benzanilide	$A = 2.754 \cdot 10^9 c - 1.129 \cdot 10^5$	0.998
Thiobenzanilide	$A = 3.384 \cdot 10^9 c + 4.065 \cdot 10^4$	0.998
2-Phenylbenzothiazole	$A = 1.201 \cdot 10^9 c - 4.260 \cdot 10^4$	0.999
Bis(N-phenylbenzimidoyl) sulfide	$A = 3.543 \cdot 10^7 c + 6.879 \cdot 10$	0.999
Bis(N-phenylbenzimidoyl) disulfide	$A = 1.325 \cdot 10^8 c - 2.179 \cdot 10^3$	0.999

A-peak area, c-concentration in mol/L.

Table 3. Statistical data of low concentration calibration curves of investigated compounds

Compound	Regression equation	R^2	SD	LOD (mol/L)	LOQ (mol/L)
Thiobenzanilide-S-oxide 254 nm	$A = 8.718 \cdot 10^8 c - 2163.2$	0.998	1197.788	$6.707 \cdot 10^{-6}$	$2.236 \cdot 10^{-5}$
344 nm	$A = 1.384 \cdot 10^9 c - 5528.1$	0.999	1899.734	$4.116 \cdot 10^{-6}$	$1.372 \cdot 10^{-5}$
Benzanilide	$A = 3.561 \cdot 10^9 c - 8161.8$	0.999	1872.305	$1.577 \cdot 10^{-6}$	$5.258 \cdot 10^{-6}$
Thiobenzanilide	$A = 4.376 \cdot 10^9 c + 2938.7$	0.999	1511.013	$1.036 \cdot 10^{-6}$	$3.453 \cdot 10^{-6}$
2-phenylbenzothiazole	$A = 1.338 \cdot 10^9 c + 270.56$	0.999	1152.494	$2.583 \cdot 10^{-6}$	$8.611 \cdot 10^{-6}$
Bis(N-phenylbenzimidoyl) sulphide	$A = 3.620 \cdot 10^7 c - 251.37$	0.999	284.785	$2.36 \cdot 10^{-5}$	$7.87 \cdot 10^{-5}$
Bis(N-phenylbenzimidoyl) disulfide	$A = 1.184 \cdot 10^8 c + 484.38$	0.998	1030.958	$2.61 \cdot 10^{-5}$	$8.71 \cdot 10^{-5}$

A-peak area, c-concentration in mol/L.

solution was not explored in the studied oxidation reaction because of the absence of thiobenzanilide-S-oxide, which appears as an intermediate in the reaction with a very short life.

In this work, the chromium(VI) oxidation of thiobenzanilide was carried out under acidic conditions with standard chromium trioxide-sulfuric acid solution, in the presence of co-solvent acetone, which increases its oxidizing power. It is known that the alkaline CrO_4^- has a reduced oxidizing power, while strong acids enhance the oxidizing power of Cr(VI). The electrode potential of chromium trioxide determined electrochemically in acetone is higher than that of the electrode potential measured in water at the same condition.[15]

Continuing our investigation on Jones' oxidation of thiobenzanilide, the influence of the concentration of Jones' reagent was studied. Because of the instantaneous reaction and strong acidic conditions, first, the Jones' reagent was diluted. Then the conditions were changed using an excess of oxidant in several molar ratios. The proposed HPLC method was used for monitoring the oxidation of thiobenzanilide, directly from the reaction mixture. As can be seen from Figure 2, three peaks appear in the chromatograms of the

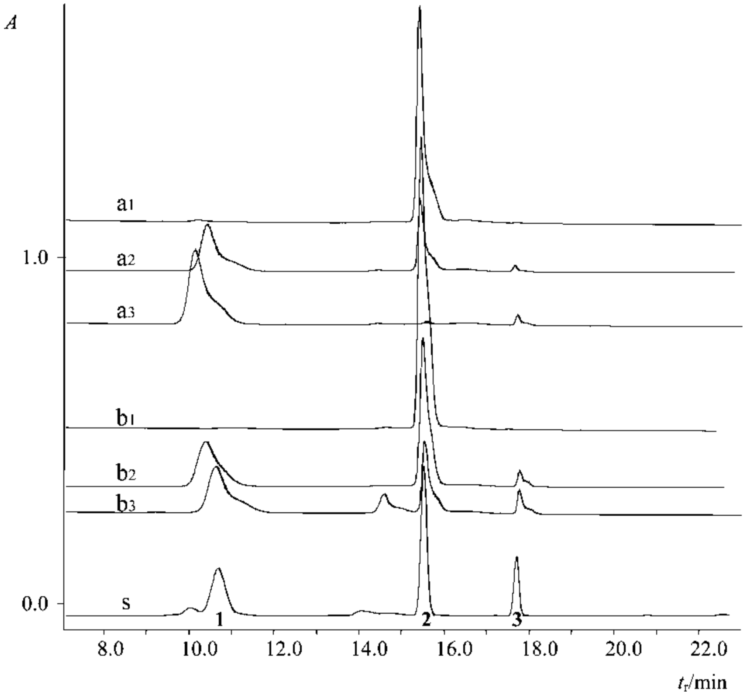

Figure 2. Chromatograms at 254 nm of: s) a standard mixture with: 1) benzanilide; 2) thiobenzanilide, and 3) 2-phenylbenzothiazole, and of reaction mixtures obtained for molar ratio substrate/oxidant: a) 1:8, and b) 1:4, where the subscripts indicate: 1) injection immediately after mixing the reagents; 2) after 3 hours, and 3) after 24 hours.

Table 4. Results obtained for thiobenzanilide, benzanilide and 2-phenylbenzothiazole in the reaction mixture for different molar ratios and periods

Molar ratios substrate/ oxidant	t/h	Thiobenzanilide (conc., mol/L)[a]	Benzanilide (conc., mol/L)	2-Phenylbenzothiazole (conc., mol/L)
1 : 2	0	$6.085 \cdot 10^{-4}$	$5.243 \cdot 10^{-5}$	LOD < c < LOQ
	3	$4.433 \cdot 10^{-4}$	$1.722 \cdot 10^{-4}$	$8.801 \cdot 10^{-5}$
	24	$5.048 \cdot 10^{-4}$	$1.938 \cdot 10^{-4}$	$9.940 \cdot 10^{-5}$
1 : 4	0	$7.340 \cdot 10^{-4}$	$5.653 \cdot 10^{-5}$	$4.369 \cdot 10^{-5}$
	3	$3.263 \cdot 10^{-4}$	$3.268 \cdot 10^{-4}$	$1.160 \cdot 10^{-4}$
	24	$1.568 \cdot 10^{-4}$	$3.379 \cdot 10^{-4}$	$1.523 \cdot 10^{-4}$
1 : 6	0	$4.845 \cdot 10^{-4}$	$5.500 \cdot 10^{-5}$	$5.312 \cdot 10^{-5}$
	3	$2.003 \cdot 10^{-4}$	$3.200 \cdot 10^{-4}$	$1.054 \cdot 10^{-4}$
	24	$1.346 \cdot 10^{-5}$	$4.743 \cdot 10^{-4}$	$1.482 \cdot 10^{-4}$
1 : 8	0	$4.541 \cdot 10^{-4}$	$6.644 \cdot 10^{-5}$	$5.240 \cdot 10^{-5}$
	3	$1.630 \cdot 10^{-4}$	$3.313 \cdot 10^{-4}$	$7.499 \cdot 10^{-5}$
	24	<LOD	$5.024 \cdot 10^{-4}$	$1.018 \cdot 10^{-4}$

[a] Initial concentration of thiobenzanilide (substrate) $= 1.00 \cdot 10^{-3}$ mol/L.

reaction mixture due to the presence of thiobenzanilide, benzanilide, and 2-phenylbenzothiazole, except for the top chromatogram where the peak from thiobenzanilide is missing (the substrate has been completely transformed in the presence of high excess, 1:8, of Jones' reagent, after 24 hours). The results obtained for the detected thiobenzanilide, benzanilide, and 2-phenylbenzothiazole immediately after mixing the reagents, and after 3 and 24 hours, are given in Table 4 for four various molar ratios substrate/oxidant.

The results obtained by monitoring the oxidation reaction by the developed HPLC method indicate that the oxidation of thiobenzanilide with Jones' reagent is not simple process and probably involves at least two side reactions: the main reaction is desulfuration of thiobenzanilide giving amide–benzanilide and sulfur; and a minor pathway is oxidative cyclization of thiobenzanilide, formed heterocyclic 2-phenylbenzothiazole. As can be seen from the results, the oxidation of thiobenzanilide starts immediately after mixing the substrate and oxidant, and the substrate is practically not detectable after 24 hour when using the molar ratio 1:8, substrate/oxidant. It is also evident that increasing the excess of the Jones' reagent favors formation of benzanilide, and at the same time, minor concentration of 2-phenylbenzothiazole is obtained.

CONCLUSION

All these conclusions, based on the results obtained using reversed phase HPLC for separation and determination of thiobenzanilide and its oxidation products, demonstrate the potential of this technique to be used for monitoring the reactions in organic synthesis. The proposed method is very simple and suitable for monitoring the oxidation of thiobenzanilide by injecting samples directly from the reaction mixture, which gives the opportunity for studying oxidation of this substrate with various oxidants in different solvents and reaction conditions.

REFERENCES

1. Naumov, P.; Anastasova, F.; Drew, G.B.M.; Ng, S.W. The crystal structure of N-ethylisatin. Bull. Chem. Technol. Macedonia **2002**, *21*, 165.
2. Naumov, P.; Anastasova, F. Experimental and theoretical FT infrared study of bis(isatinato)mercury(II): Correlation with the structure. Bull. Chem. Technol. Macedonia **2000**, *19*, 3.
3. Naumov, P.; Anastasova, F. Experimental and theoretical vibrational study of isatin, its 5-(NO_2, F, Cl, Br, I, and CH_3) analogues and the isatinato anion. Spectrochimica Acta Part A **2001**, *57*, 469.
4. Naumov, P.; Anastasova, F.; Drew, G.B.M.; Ng, S.W. 5-fluoroindoline-2,3-dione. Acta Cryst. **2000** (C56), e406.
5. Juranić, Z.; Anastasova, F.; Juranić, I.; Stanojković, T.; Radulović, S.; Vuletić, N. Antiproliferative action of isatine-β-thiocarbohydrazone and N-ethylisatine-β-thiocarbohydrazone on human PBMC and on two neoplastic cell lines. J. Exp. Clin. Cancer Res. **1999**, *18* (3), 317.
6. Jovevska, L.; Anastasova, F.; Aleksić, V. The synthesis of some N-[4-substituted phenyl]-3-acetoxythiobenzamides and their N^1 and N^3-disubstituted amidrazones. Synth. Commun. **1996**, *26*, 279.
7. Kunes, J.; Jachym, J.; Jiraško, P.; Odlerova, Z.; Waisser, K. Combination of Topliss approach with Free-Wilson analysis in the study of antimycobacterial activity of 4-alkylthiobenzanilides. Collect. Czech. Chem. Commun. **1997**, *62*, 1503.
8. Gabriel, J.; Nemec, I.; Zimova, N.; Hanus, V.; Waisser, K. Electrochemical oxidation of thiobenzanilide. Electroanalysis **1994**, *6*, 75.
9. Kresta, J.; Kastner, P.; Klimeš, J.; Klimešova, V. Reversed-phase high-performance liquid chromatographic determination of lipophilicity of potential antituberculotic compounds. J. Liq. Chromatogr. Rel. Technol. **2004**, *27* (15), 2539.
10. Walter, W.; Voss, J. The chemistry of thioamides. In *The Chemistry of the Functional Groups*; Zabicky, J., Ed.; Interscience Publishers: London, 1970; 439.
11. Schaeffer, J.R.; Goodhue, C.T.; Risley, H.A.; Stevens, R.E. The synthesis, stability, and sulfur-elimination reactions of some bis(N-arylimidoyl) disulfides. J. Org. Chem. **1967**, *32*, 392.
12. Hodosan, F.; Serban, N. The reactions of diacyl peroxides. III. The mechanism of formation of N-phenylbenzamide by the action of Bz_2O_2 on thiobenzanilide in the molten state. Bull. Soc. Chim. France **1959**, 507.
13. Podolešov, B.; Bogdanov, B. Oxidation of thiobenzanilide with phenyliodoso diacetate. Glas. Hem. Drus. Beograd **1981**, *46* (3), 11.
14. Walter, W.; Curts, J.; Pawelzik, H. The oxidation products of thioamides. Just. Lieb. Ann. Chem. **1961**, *643*, 29.

15. Cainelli, G.; Cardillo, G. Reactivity and structure concepts in organic chemistry. In *Chromium Oxidations in Organic Chemistry*; Hafner, K., Rees, W.C., Trost, M.B., Lehn, J.-M., Schleyer, P., von, R., Zahradnik, R., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, Tokyo, 1984.
16. Fišer-Jakić, L.; Karaman, B.; Jakopčić, K. Thioamides. XV. Some new substituted 2-(2- or 3- furyl)-benzothiazoles. The preparation and properties. Croat. Chem. Acta **1980**, *53* (1), 69.
17. Ristovska, N.; Anastasova, F. Synthesis of bis(N-phenylbenzimidoyl) disulfide in the presence of $CaCO_3$. In *Book of Abstracts*; XVIII Congress of Chemists and Technologists of Macedonia; Ohrid, Republic of Macedonia, Sept 23–25, 2004; 153.

Received February 15, 2005
Accepted March 31, 2005
Manuscript 6609