

FATTY ACID COMPONENTS OF *BUTHUS SINDICUS* (SCORPION)

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Fatty acid components of lipid contents of *Buthus indicus* (Scorpion) have been characterized by mass spectrometry and GCMS techniques during prehibernation period (July-Oct.) and their fragmentation pattern has been discussed.

**Key words:** Fatty acids, *Buthus indicus*, GCMS

## INTRODUCTION

The living animal cell is a complex energy matter nexus, which plays a vital role in the normal organomechanical functioning. In this connection particular mention could be made of hibernating animals. Hibernation is a physiological adaptation markedly linked with changes in the distribution of lipid in body tissues [1,3]. Since the energy requirement of the hibernating animal is believed to be met mostly by the body fat [4,5]. It was considered of interest to identify the fatty acids, components of lipid contents [6,7] via mass spectrometry that has long been used as a unique tool both for skeletal assignments and for recognition and characterization of natural products. A number of reports are available on the mass fragmentation pattern of saturated and unsaturated fatty acids [8,12].

In the present preliminary study, the component fatty acids of total lipid contents of *Buthus indicus*, a scorpion commonly found in tropical countries, have been characterized through mass spectrometry and GCMS technique.

## EXPERIMENTAL

Scorpions collected from suburban area of Karachi were exhaustively extracted with hexane in a Soxhlet apparatus for two days. The hexane extract was shaken out with 90% methanol to remove the steroidal compounds. The hexane-phase was washed with water dried with anhydrous  $\text{Na}_2\text{SO}_4$  and freed of the solvent under reduced pressure. The residue (7.9% of the total weight of scorpion) thus obtained was refluxed with 5% methanolic KOH and shaken out with ethyl acetate to remove the saponifiable matter. The lower alkaline phase was acidified and free fatty acids were extracted out with ethyl acetate. After usual workup, the residue was esterified with methanol in presence of  $\text{H}_2\text{SO}_4$ . Methyl esters of scorpion fatty acids

were analysed through GCMS on a Varian Model 3700 capillary gas chromatograph attached with a MAT 112 mass spectrometer connected to PDP 11/34 computer system.

## RESULTS AND DISCUSSION

The GCMS spectrum showed 14 molecular ion peaks, 11 of which were saturated, 2 mono-unsaturated and 1 di-unsaturated methyl esters. These results and characteristic mass fragments observed in mass spectra are given in Table 1. The diagnostic peaks observed in the case of saturated fatty acid esters were molecular ion peak ( $\text{M}^+$ ),  $\text{M}^+ - 31$  resulting from the loss of methoxy group,  $\text{M}^+ - 43$  and  $\text{M}^+ - 59$  arising from the loss of methoxy group and two hydrocarbon units ( $2\text{CH}_2$ ). In methyl esters of mono-unsaturated and di-unsaturated fatty acids the diagnostic

Table 1. Mass spectral data for fatty acid esters of total lipid contents of *Buthus indicus*  
m/z (rel. intes. %)

$\text{M}^+$	$\text{M}^+ - 31$	$\text{M}^+ - 43$	$\text{M}^+ - 59$	$\text{M}^+ - 74$	Fatty acid
130(8)	99(10)	87(25)	71(50)	—	Hexanoic
158(7)	127(6)	115(22)	99(18)	—	Octanoic
186(6)	155(6)	143(13)	127(8)	—	Decanoic
214(12)	183(8)	171(5)	155(10)	—	Dodecanoic
242(6)	211(9)	199(6)	183(10)	—	Tetradecanoic
270(10)	239(6)	227(18)	211(12)	—	Hexadecanoic
294(5)	263(8)	—	—	220(5)	Octadecadienoic
296(2)	265(10)	—	—	222(9)	Octadecenoic
298(10)	267(12)	255(9)	239(6)	—	Octadecanoic
326(14)	295(3)	283(6)	267(5)	—	Eicosanoic
352(2)	221(5)	—	—	278(4)	Docosenoic
354(4)	323(10)	311(1)	295(3)	—	Docosanoic
396(2)	365(5)	353(4)	337(1)	—	Pentacosanoic
424(1)	393(4)	381(2)	365(1)	—	Heptacosanoic

mass fragments were  $M^+ - 31$  and  $M^+ - 74$ . These findings are consistent with those observed earlier [7]. Studies in hibernating and post hibernating animals would provide an insight into the physiological behaviour and lipid-energy relationship. The study is in progress and will be reported later.

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were mixed in each experiment. An anhydrous was used. The iron (II) chloride complex was prepared in solution by mixing ferrous ammonium sulphate with lithium chloride in the ratio of 1:2. Preoxidized amounts of reduced water and alcohol was added to bring the concentration of the complex to 0.001 M. The pH of the reaction mixture was maintained at 5.0 by a citric acid-sodium citrate buffer which was essential in studying the change of effects on the reaction rate by preventing the change of [Fe<sup>2+</sup>] during the oxidation process because the oxidation of iron (II) is quite sensitive to [H<sup>+</sup>]. The present work as well as the previous work showed that oxygen concentration affects the rate of oxidation of iron (II) complexes. For this reason all experiments were carried out in an open bottle with constant stirring in order to replace the consumed oxygen during the reaction. The reduction of iron(II) complex was followed by determining the amount of iron (III) produced after different intervals as follows. Aliquots of the reaction mixture at certain calculated times were transferred into a brown bottle containing 5 ml of 0.1 N H<sub>2</sub>SO<sub>4</sub> to lower the pH in order to stop the oxidation process of iron (II). Then an excess amount of 0.1 M NH<sub>4</sub>NO<sub>3</sub> was added. The concentration of the red Fe<sup>3+</sup> (SCN)<sub>3</sub> iron complex was determined spectrophotometrically.

RESULTS AND DISCUSSION

The rate of the oxidation of iron(II) complex by molecular oxygen at constant pH of 5.0 were measured in various alcohol-water mixtures. The reaction was first order in iron (II). The concentration of oxygen was kept fixed during the course of reaction as described previously in the

INTRODUCTION

The oxidation of iron (II) by molecular oxygen in aqueous acidic and alkaline media has been extensively studied by many workers [1-5]. However, the study of solvent effects on such a reaction has received very little attention. Many studies dealing with the influence of changes of organic solvents on electron transfer reactions have been reported such as iron (II) and cobalt (II) with oxidizing agents. It has been reported that the rate of oxidation of iron (II) in organic solvents was strongly affected by the addition of organic solvents to the aqueous solution and this was interpreted in most cases as being due to changes in the solvation of the reactant species or the reactant metal ion as well as the oxidizing complex.

The aim of this paper is to evaluate the effects of alcohols such as methanol, ethanol and isopropanol on the oxidation of iron (II) complex by molecular oxygen in water-alcohol mixtures. The study of this reaction is of interest because of its relation to the biologically occurring reaction of iron (II) complex with oxygen which is related to iron (II) complex. Moreover, the Fe<sup>3+</sup> complex is related to the enzyme (catalase) which catalyzes the reaction of hydrogen peroxide which produces Fe<sup>3+</sup> as the active ion of its catalytic activity [6].

EXPERIMENTAL

Reagent grade chemicals and redistilled water were used throughout. All solutions were prepared freshly. The reaction of ferrous (iron (II) complex) with oxygen was studied in the following manner: 5 ml of 0.1 N H<sub>2</sub>SO<sub>4</sub> was added to 5 ml of 0.001 M iron (II) complex and the reaction was followed at 25°C.