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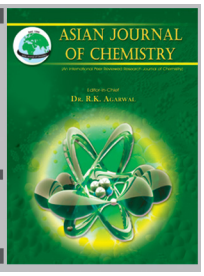

NOTE

Preparation and Structural Characterization of L-Arginine-selenic Acid Addition Compound

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Seleno-arginine was synthesized using arginine and selenium dioxide and its conventionally chemophysical properties were analyzed. The structure of the product was determined by high performance liquid chromatography, Fourier transform spectrometer, mass spectra and nuclear magnetic resonance spectroscopy.

Key Words: Selenoarginine, Preparation, Structural characterization.

Selenium is an essential micronutrient for humans and animals. As a key component of a number of functional selenoproteins required for normal health, selenium has a large number of biological functions. Selenium was suggested to be mediated through the glutathione peroxidases (GPx) that removed potentially damaging lipid hydroperoxides and hydrogen peroxide. At least five of these peroxidases have now been identified as operating in different cell and tissue compartments[1,2]. Thus, selenium can act as an antioxidant in the extracellular space, the cell cytosol, in association with cell membranes and specifically in the gastrointestinal tract, all with potential to influence immune processes[3]. So selenium deficiency is associated with many diseases[4,5], such as chronic heart failure[6,7] skeletal muscle myopathy and neurogenic disease cretinism (in iodine-deficient populations) and more marginal deficiencies may contribute to reduced immune function, some cancers and viral diseases[8].

Generally, organic selenides have a better biological security, absorption and utility than inorganic selenides. Therefore, there are important significance to seek secure organic selenides for human health. Previous studies demonstrated that L-arginine-selenic acid (selenoarginine) possessed an better antioxidation effects than SeO_2 in CCl_4-induced liver injury mice and alcohol-induced liver injury mice and D-gal treated mice as experimental senile model[9-11]. Herein,we report the highly efficient synthesis and the structural features of seleno-arginine from commercially available L-arginine and SeO_2.

L-Arginine and SeO_2 were purchased from Sigma Co. All other reagents were of grade AR.

The preparation of the selenoargine was based on the synthesis method as shown in **Scheme-I**. The selenoargine was synthesized by L-arginine and selenium dioxide (1:0.8, molar ratio) at low-temperature vacuum in 10 % H_2O_2. The white powder was obtained after precipitated and washed by absolute ethanol and the yied is 91 %.

$$SeO_2 \rightarrow (Arg)_2H_2SeO_3$$

Scheme-I

Melting points was determined with a Büchi model 510 m.p. apparatus. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. IR (KBr-disks) spectra were recorded by Brucker Tensor 27 spectrometer. Mass spectra were recorded on a Q-TOF Global mass spectrometer with a JASCO P-1020 polarimeter. ^1H and ^{13}C NMR spectra were taken on a Bruker A.G, AVIII400/600MHz spectrometer with tetramethyl-silane (TMS) as internal standard and chemical shifts values are recorded.

High pressure liquid chromatograph (HPLC): 10 mg of selenoargine were dissolved in 5 mL phosphate buffer (pH 7.5) and fltered through a 0.22 μm Millipore flter, applied to a HPLC system equipped with RP-C18 column (4.6 mm × 250 mm, column temperature 30 ºC) and RF-535 fluorescence Detector. A sample solution (20 μL) was injected and eluted with acetonitrile/water (65:35, v/v) at a flow rate of 1.0 mL/min.

The selenoargine was efficiently synthesized in good yields from the L-arginine and selenium dioxide. Analytic data of chemophysical parameters of Arg and selenoargine were shown Table-1.

TABLE-1
CHEMOPHYSICAL PARAMETERS OF Arg AND SELENOARGINE

Parameters	Arg	Selenoargine
Appearance	White crystal	White powder
Transmittance (%)	98.9	99.2
$[\alpha]_D^{25}$	+26.5°	+17.6°
m.p. (°C)	226.7	126.2
Dissolubility	Soluble in water	Easily soluble in water

ESI-MS m/z: 479.26 $[M + H]^+$ (calculation for selenoargine, 478.14), elemental analysis for selenoargine: calcd. (%) C, 30.19; H, 6.33; N, 23.47; O, 23.46; Se, 16.54; Found (%) C, 30.18; H, 6.34; N, 23.48; Se, 16.54.

The FTIR spectrum of selenoargine (Fig. 1) showed obvious absorptions at 1047 and 869 cm^{-1} which are the characteristic absorptions of Se-O and Se=O. The data of IR analysis of the selenoargine were showed as follows: 3384 ν(NH), 2963 ν(C-H), 1575, 1407 ν(COO-), 1258, 1048 ν(C-N), 1047 ν(Se-O), 869 ν(Se=O).

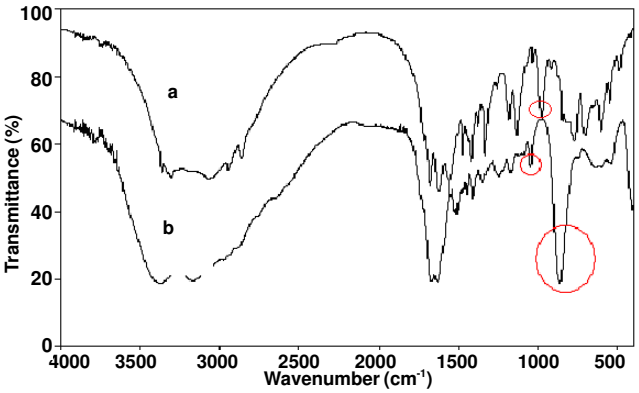


Fig. 1. Infrared absorption spectra of a: Arg and b: selenoargine

The result of HPLC analysis (Fig. 2) indicated that the retention time of the product was 13.7 min which was much more advanced than arginine's 16 min. The data of NMR analysis of selenoargine were showed in Table-2.

In summary, the conventionally chemophysical parameters of selenoargine were obviously different from arginine. The result of HPLC analysis showed that the retention time of the product was 13.7 min which was much more advanced than arginine's 16 min; FTIR showed that the product had two characteristic absorptions at 1047and 869 cm^{-1}, due to Se-O

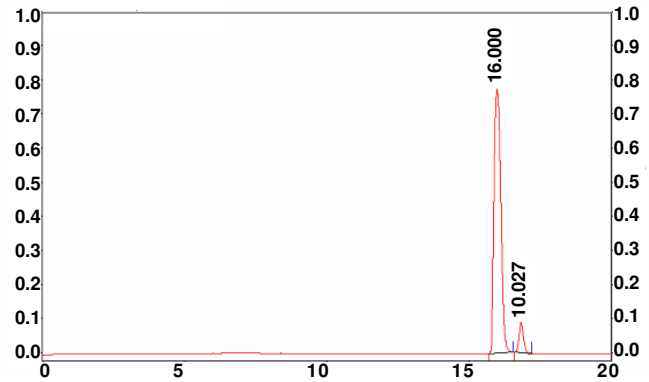
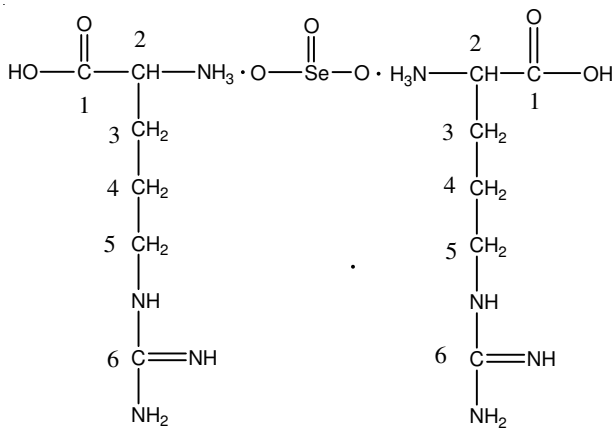


Fig. 2. HPLC analysis of Arg and selenoargine: (a) Arg (b) ASe

TABLE-2
DATA OF NMR ANALYSIS OF Arg AND SELENOARGINE

Position	^{1}H NMR (signals at ppm)		^{13}C NMR (signals at ppm)	
	Arg	Selenoargine	Arg	Selenoargine
1	–	–	183.22	173.44
2	3.04	3.89	55.65	53.78
3	1.45	1.97	31.74	27.46
4	1.39	1.75	24.59	24.00
5	3.02	3.29	41.07	40.61
6	–	–	156.85	157.01

and Se=O bond stretchings, respectively. Structure of the product was confirmed by results of ^{1}H and ^{13}C NMR: SeO_3^- was added on C_2 position in the primary amidocyanogen of arginine molecule. The analytic data of lead to the conclusion that the structure of the synthesized compound is formed by L-arginine and seleninic acid in the ratio of 2:1. The structure was shown as **Scheme-II**.



Chemical Formula: $C_{12}H_{30}N_8O_7Se$
Exact Mass: 478.14

Scheme-II

ACKNOWLEDGEMENTS

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