Synthesis and Identification of New Organoselenium Compounds Derived from 4-(Chloromethyl)-2-Hydroxybenzaldehyde

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Abstract

The present study involved the preparation of organoselenium compounds derived from salicylaldehyde by reacting between 4-(chloromethyl)-2-hydroxybenzaldehyde and selenium metal with presence sodium cyanide in dimethyl sulphoxide under nitrogen gas to obtain 2-hydroxy-4-(selenocyanatomethyl)benzaldehyde then reacted with iodide to produced 2-hydroxy-4-((triiodo-l4-selaneyl)methyl)benzaldehyde. all compounds were identified by the infrared spectrum (IR), the mass spectroscopy (MASS) and the nuclear magnetic resonance spectrum (1HNMR). The results agreement with the suggested chemicals structures.

Keywords: Organoselenium, Selenium Metal, Benzaldehyde and Sodium Cyanide.

Introduction

Selenium is an element in the active sites of certain enzymes such as amino acid enzymes for selenomethionine and selenocysteine [1-5]. Organic compounds, in general, are of great importance because of their active biological potential, such as antivirals, antihypertensives, antioxidants, antimicrobial properties, anti-tumor [6-12] Interestingly, among organoselenium compounds, silicanite derivatives have shown promising chemical protection for certain types of cancer[13].

In addition to possessing the properties of good chemical protection, organic selenocytes were found to be useful antioxidants [14-16] Organic selenium compounds have been tested as antibacterial, antiviral, antifungal, anti-parasite, anti-inflammatory and anti-histamine[17]these compounds can be used as protective chemical agents on the colon and breast tumors[18-20]. Selenium contains fragments that can easily be incorporated into the organic compound. Selenium can also be removed by several transformations such as oxidation, leading to the formation of a double bond via the synthesis of selenium oxide[21] In order to prevent the ability of oxidation of peroxide of fat in the human body must be maintained the work of an enzyme containing selenium, clotathione and peroxidase, which stimulates the reactions of peroxy with compounds of the group of sulfanil in Clotathione[22] Organic selenium compounds have been widely used in biochemistry, medical chemistry, organic synthesis and materials science for their unique chemical and biological activities[23-27] Recently, the chemistry of organic selenium compounds has been addressed as environmentally friendly[28-34].

Experimental

Chemicals and Apparatus

Chemicals acquired from Sigma-Aldrich, Fluka and BDH utilized without filtration. Liquefying point was dictated by utilizing open hairlike tube dissolving point mechanical assembly. ^{1}H NMR spectra was recorded onBruker DRX System AL (500 MHz)with TMS as an inner reference utilizing DMSO-d_6 dissolvable. Infra-red spectra were recorded with KBr circles utilizing a FT- IR spectrophotometer Shimadzu model 8400 S in reach 4000- 250 cm^{-1}. Dissolving purposes of every single strong compound were resolved utilizing a MPS10 electrically warmed liquefying point mechanical assembly.

[2-hydroxy-4-(selenocyanatomethyl) benzaldehyde]

Selenium metal (0.0056 mol, 0.44 g) and dried sodium cyanide (0.0056 mol, 0.27 g) was mixed together in (15 ml) of freshly distilled dimethylsulfoxide and reflux for 1 hour at 100 ˚C under nitrogen. Cooled the mixture of reaction then added 15 mL of dry dimethylsulfoxide to the solution and leave to cool at room temperature, where pale - yellow solution was obtained thenadded (0.0058 mole, 1 gm) of 4-(chloromethyl)-2-hydroxybenzaldehyde and reflux for two hours.cool to room temperature, then pour product into a 250 ml of cool distilled water. Pale yellow crystalswas

formed. wash with water and ethanol. Re-crystallized using ethanol (melting point: 178-180C°, yield: 57%)

[2-hydroxy-4-((triiodo-l4-selaneyl) methyl) benzaldehyde]

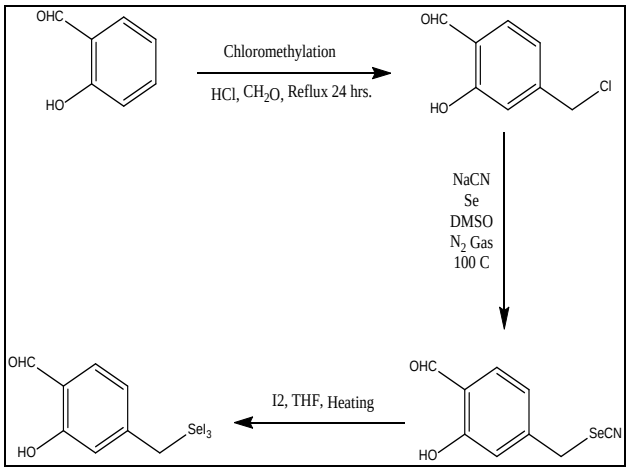
Dissolve (0.002mol, 0.5g)of 2-hydroxy-4-(selenocyanatomethyl) benzaldehyde in 50 ml of tetrahydrofuran then Add(0.002 mol, 0.25 g) of iodine dissolved in tetrahydrofuran and heated the mixture. Cool and leave in a dark place for 24 h, brown crystals have been appeared, collect and dry the crystals recrystallized by using ethanol. (Melting point: 261-263, yeild37%)

Table- 1: Physical data for organoselenium compounds

No	Molecular formula	M.Wt	Color	m.p. C°	Yield %
1	$C_9H_7O_2NSe$	`239.96	Pale-Yellow	178-180	57%
2	$C_8H_7O_2SeI_3$	595	Brown	261-263	37%

Results and Discussion

The compound 4-(chloromethyl)-2-hydroxybenzaldehyde is formed by the chloromethylation for salicylaldehyde under reflux for 24 hrs., the reaction gave a great yield of starting material. [2-hydroxy-4-(selenocyanatomethyl)benzaldehyde] has been obtained by reacting between 4-(chloromethyl)-2-hydroxybenzaldehyde and sodium cyanide and selenium metal in DMSO under N_2 gas, such as Scheme (1)

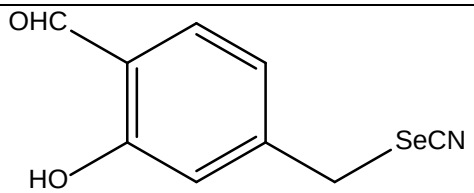
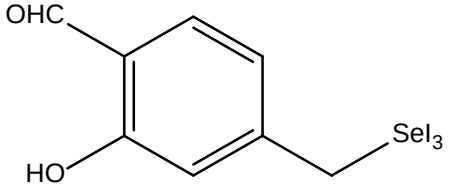


Scheme (1) preparation of compounds [2-hydroxy-4-(selenocyanatomethyl)benzaldehyde] and [2-hydroxy-4-((triiodo-l4-selaneyl)methyl)benzaldehyde]

The spectral measurements of ^{1}HNMR for ***[2-hydroxy-4 (selenocyanatomethyl) benzaldehyde]*** as shown in Figure (3) and Table (2),showed a CH_2triplet signal centered at (4.42ppm),[35, 36] while the aromatic protons appeared multiple signal at the range(6.92 - 7.61 ppm).[35, 36]A triplet signal centered at 10.23 ppm due to phenolic proton for OH. While CH for aldehyde appeared as singlet signal at 10.69 ppm.[35, 36]The spectral measurements of ^{1}HNMR for ***[2-hydroxy-4- ((triiodo-l4-selaneyl) methyl) benzaldehyde]*** as shown in Figure (4) and Table (),showed a singlet signal for CH_2 centered at (4.28 ppm),[35, 36] the protons for aromatic ring appeared at 7.64 ppm and 8.03 ppm.[35, 36]A singlet signal appeared at 10.23 ppm due to phenolic proton for OH.

CH in aldehyde centeredat 10.74 ppm as singlet signal.[35, 36]

Table- 2: ^{1}H NMR Spectral Data for Selected Compounds

	Structure for comp.	^{1}H NMR (DMSO-d_6); TMS = 0 ppm
1		6.92 - 7.61 (m, 3H, Ar-H); 4.42 (t, 2H, CH_2-Se); 10.23 (t, 1H, OH); 10.69 (s, 1H, CHO)
2		7.64 & 8.03 (s - s, 3H, Ar-H); 4.28 (s, 2H, CH_2-Se); 10.23 (s, 1H, OH); 10.74 (s, 1H, CHO)

IR spectra for all compounds displayed common features in certain regions and characteristic bands in the fingerprint and other regions. The IR spectra confirm the suggested structure for organoselenium compounds.[35, 36] As shown in Figure (1) and (2), Table (3).

In the IR spectrum, we observe a clear beam at (3317 $cm^{-1}$and 3363 cm^{-1}) respectively refer to phenolic OH[35, 36] in selenocyanate and iodoorganoselenium derivatives, the appearance of a band at (2059cm^{-1}) respectively indicated to C≡N bond for selenocyanate, and the aromatic C-H[35, 36] appeared at (3062 cm^{-1}3209 cm^{-1}) respectively for selenocyanate and iodoorganoselenium derivatives, the C-H aliphatic, obtained at (2931 $cm^{-1}$and 2916 cm^{-1}) respectively for selenocyanate and iodoorganoselenium derivatives, while the C = O group shows a very clear band at (1712 cm^{-1}), band appeared at (1651 cm^{-1} and 1658 cm^{-1})[35, 36]respectively respectively for selenocyanate and iodoorganoselenium derivatives, refer to C=C aromatic bond.[35, 36]

Table -3: FT - IR Spectral Data for Selected Compounds

Phenolic –OH	C≡N	Aliphatic C – H	Aromatic C – H	Carbonyl C=O	Aromatic C=C
3317	2059	2931	3062	1712	1651
3363	___	2916	3209	1712	1658

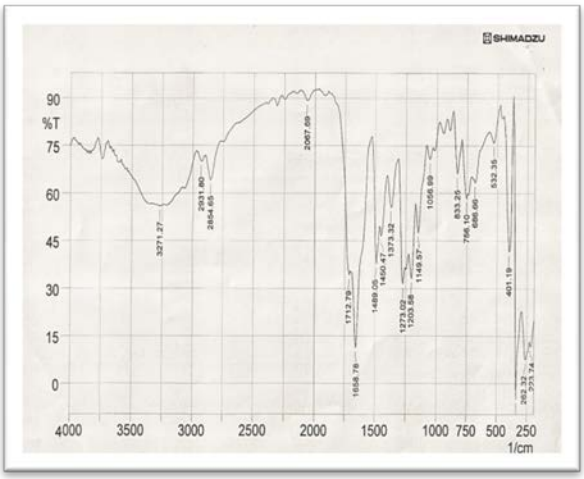


Figure - 1: IR spectrum for [2-hydroxy-4-(selenocyanatomethyl)benzaldehyde]

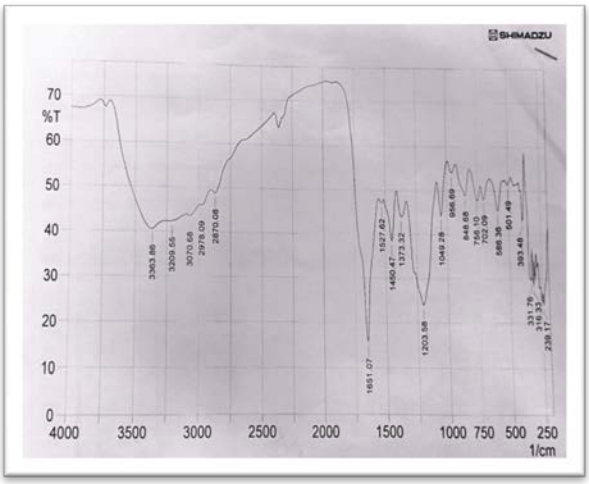


Figure -2: IR spectrum for [2-hydroxy-4-((triiodo-l4-selaneyl)methyl)benzaldehyde]

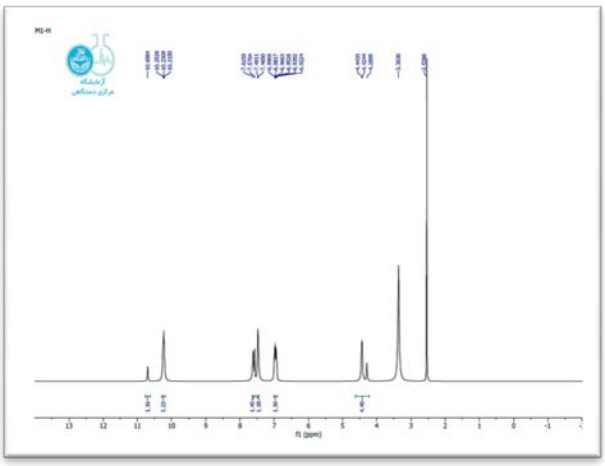


Figure- 3: ^{1}H NMR spectrum for [2-hydroxy-4-(selenocyanatomethyl)benzaldehyde]

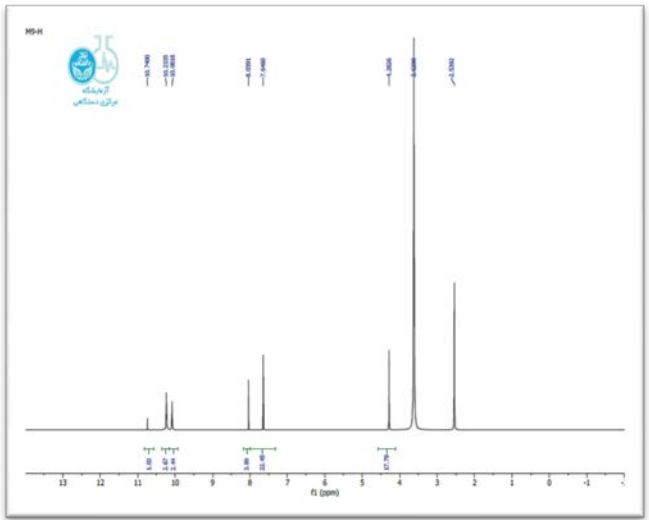


Figure- 4: ^{1}H NMR spectrum for [2-hydroxy-4-((triiodo-l4-selaneyl)methyl)benzaldehyde]

In mass spectrum for [2-hydroxy-4-(selenocyanatomethyl) benzaldehyde] and [2-hydroxy-4-((triiodo-l4-selaneyl) methyl) benzaldehyde] showed the molecular ion in (240 m / z) and (595 m /z) respectively (35, 36). fragments shown as Figure (5), Figure (6), Table (4), Table (5), Scheme (2) and Scheme (3) respectively.

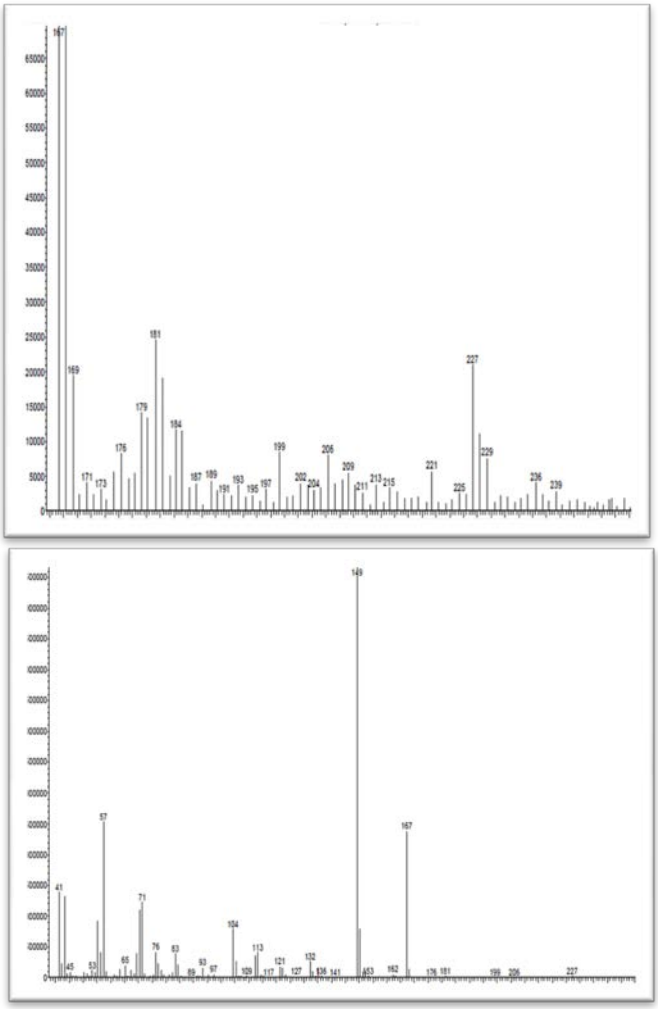


Figure -5: Mass spectrum for [2-hydroxy-4-(selenocyanatomethyl)benzaldehyde]

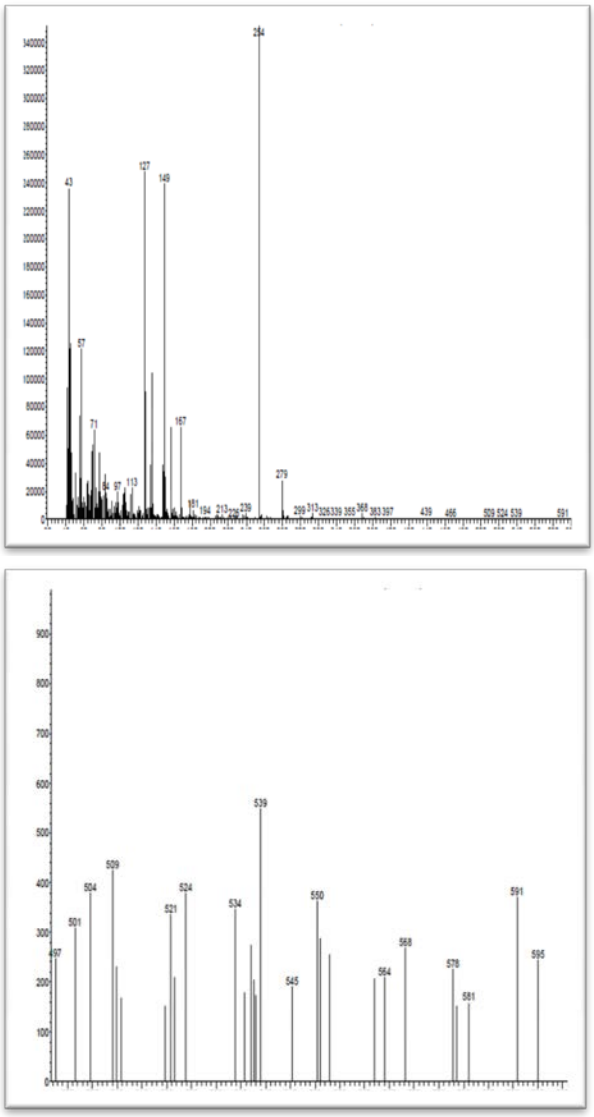
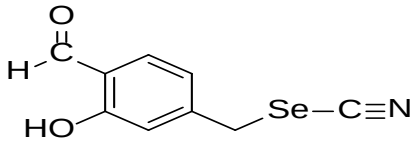


Figure -6: Mass spectrum for [2-hydroxy-4-((triiodo-l4-selaneyl)methyl)benzaldehyde]

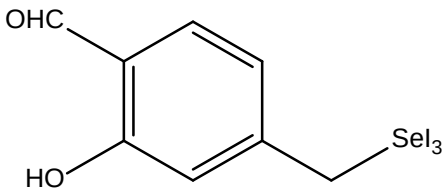
Table -4: Fragments for 2-hydroxy-4-(selenocyanatomethyl)benzaldehyde



2-hydroxy-4-(selenocyanatomethyl)benzaldehyde

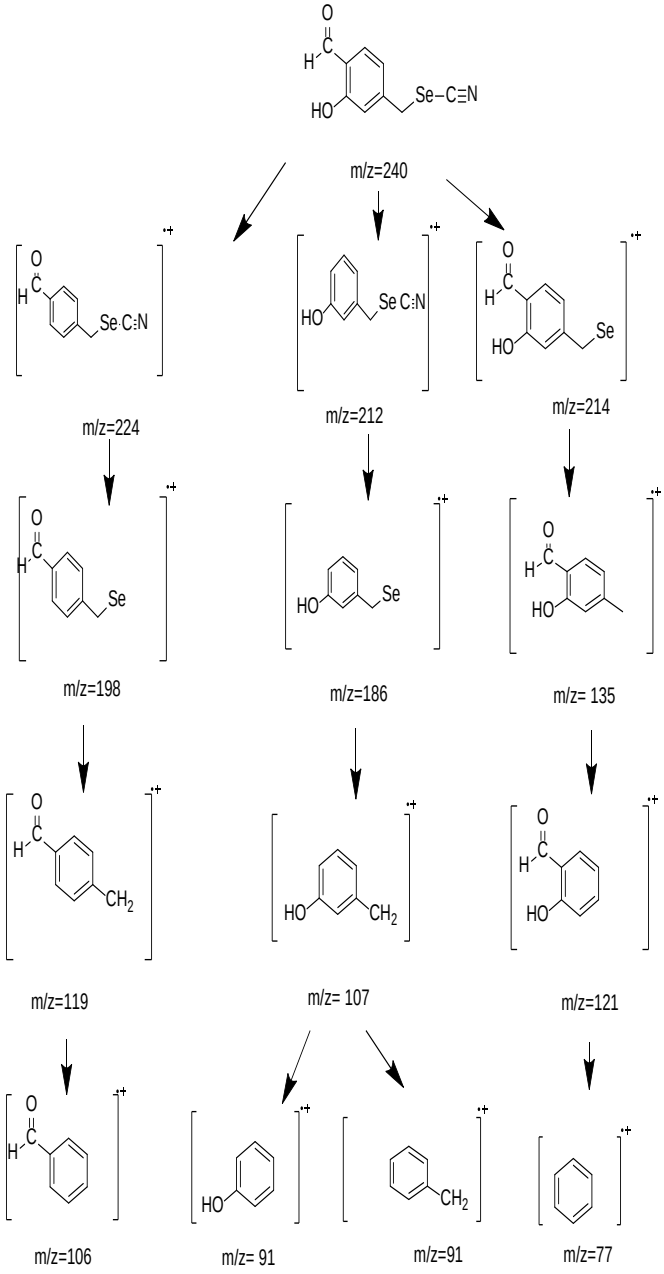
Molecular formula	m/z	Molecular formula	m/z
$[C_6H_5]^{\cdot+}$	77	$[C_7H_7OSe]^{\cdot+}$	186
$[C_7H_7]^{\cdot+}$	91	$[C_8H_7OSe]^{\cdot+}$	198
$[C_7H_6O]^{\cdot+}$	106	$[C_8H_7ONSe]^{\cdot+}$	212
$[C_7H_6O_2]^{\cdot+}$	121	$[C_8H_7O_2Se]^{\cdot+}$	214
$[C_8H_7O_2]^{\cdot+}$	135	$[C_8H_7ONSe]^{\cdot+}$	224

Table -5: Fragments for [2-hydroxy-4-((triiodo-l4-selaneyl)methyl)benzaldehyde]

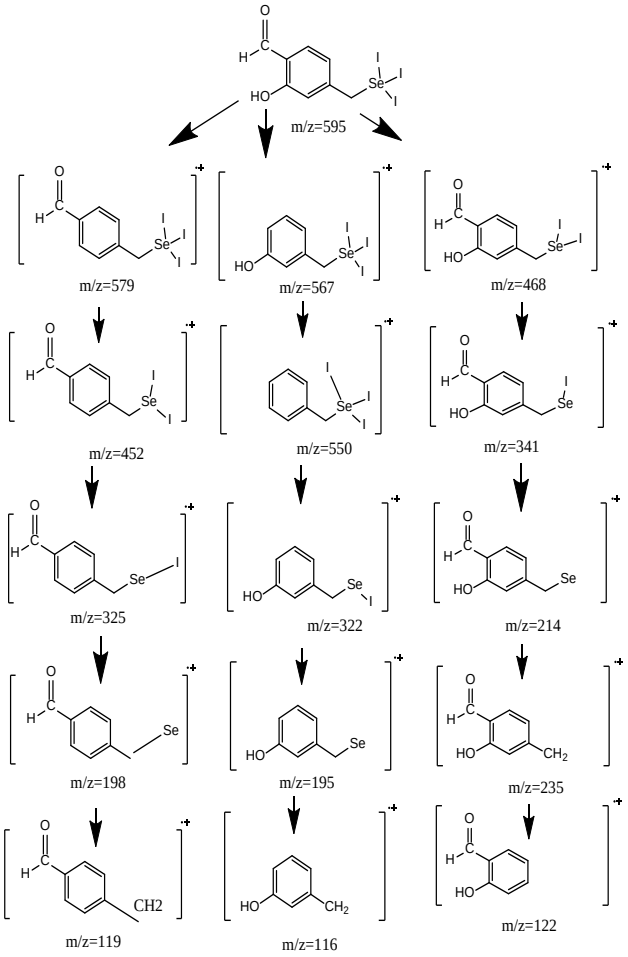


[2-hydroxy-4-((triiodo-l4-selaneyl)methyl)benzaldehyde]

Molecular formula	m/z	Molecular formula	m/z
$[C_8H_7I_3O_2Se]^{\cdot+}$	579	$[C_8H_7IO_2Se]^{\cdot+}$	341
$[C_7H_7I_3OSe]^{\cdot+}$	567	$[C_8H_7IOSe]^{\cdot+}$	325
$[C_7H_7I_3Se]^{\cdot+}$	550	$[C_8H_7O_2Se]^{\cdot+}$	314
$[C_8H_7I_2O_2Se]^{\cdot+}$	468	$[C_7H_7OSe]^{\cdot+}$	195



Scheme (2) mechanism for fragmentation for [2-hydroxy-4-(selenocyanatomethyl)benzaldehyde]



Scheme (3) mechanism for fragmentation for [2-hydroxy-4-((triiodo-l4-selaneyl)methyl)benzaldehyde]

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