

Comprehensive speciation of low-molecular weight selenium metabolites in mustard seeds by HPLC - electrospray linear trap/Orbitrap tandem mass spectrometry

Authors

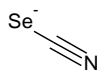
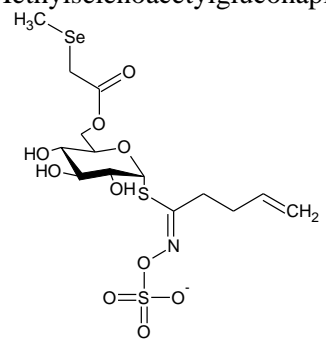
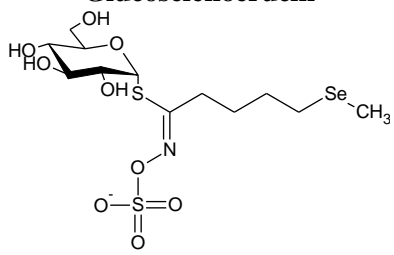
Laurent Ouerdane^{a*}, Federica Aureli^b, Paulina Flis^a, Katarzyna Bierla^a, Hugues Preud'homme^a, Francesco Cubadda^b, Joanna Szpunar^a

^a Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, CNRS UMR 5254, Université de Pau et des Pays de l'Adour, 64053 Pau, France.

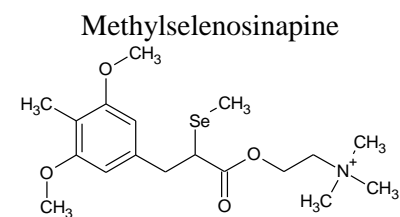
^b Istituto Superiore di Sanità, Department of Food Safety and Veterinary Public Health, Rome, Italy

Supplementary data

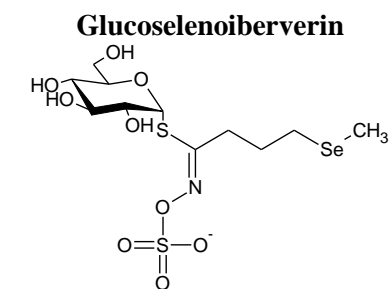
Table S1. Low molecular weight Se species identified in *Brassica nigra* seeds. Compared to Table 2, additional data are presented such as HILIC and CE retention times (glucosinolates could not be detected by CE because only water extract was analyzed), MS/MS fragment ions (for novel molecules) and compound putative structures. Major Se species are presented in bold characters.

n°	RT HILIC	RT CE	Exact mass (m/z)	Measured mass (m/z)	Error value (ppm)	Molecular formula (monocharged)	Ion. mode	Fragment ions (formula)	Fragment ions (rounded mass)	Putative structure and name when applicable
1	1.9	19.8	105.92014	105.92058	4.2	CNSe	-	/	/	(Iso)selenocyanate 
2	7.7	/	507.98555	507.98612	1.1	C₁₄H₂₂NO₁₀S₂Se	-	HSO ₄ C ₃ H ₅ O ₂ Se C ₆ H ₉ O ₈ S C ₉ H ₁₅ O ₁₀ SSe	96.96 152.95 241.00 394.95	Methylselenoacetylgluconapin 
3	19.2	/	467.99061	467.98973	-1.9	C₁₂H₂₂NO₉S₂Se	-	HSO ₄ C ₆ H ₁₁ O ₅ S C ₆ H ₁₂ NOSSe C ₆ H ₁₁ O ₉ S C ₆ H ₁₁ O ₈ S ₂ C ₆ H ₁₂ NO ₅ SSe C ₆ H ₁₁ O ₉ S ₂	96.96 195.03 225.98 259.01 274.99 289.96 290.98	Glucoselenoerucin 

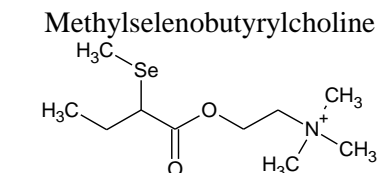
4	20.2	/	404.13355	404.13367	0.3	$C_{18}H_{30}NO_4Se$	+	$C_9H_{11}O_2$	151.08
								$C_{12}H_{20}NO_2$	210.15
								$C_4H_{18}O_4$	250.12
								$C_{17}H_{27}NO_4$	309.19
								$C_{15}H_{21}O_4Se$	345.06



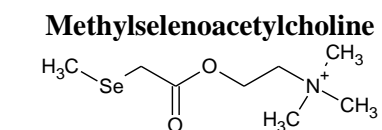
5	20.6	/	453.97496	453.97436	-1.3	$C_{11}H_{20}NO_9S_2Se$	-	HSO_4	96.96
								$C_6H_{11}O_5S$	195.03
								$C_5H_{10}NOSse$	211.96
								$C_6H_{11}O_9S$	259.01
								$C_6H_{11}O_8S_2$	274.99
								$C_5H_{10}NO_5Sse$	275.94
								$C_6H_{11}O_9S_2$	290.98

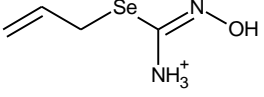
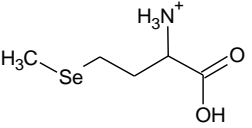
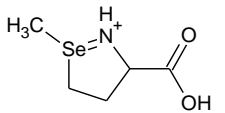
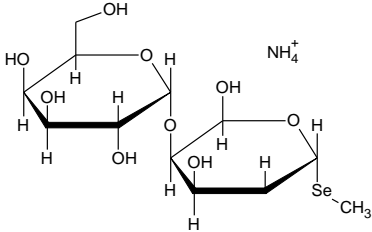
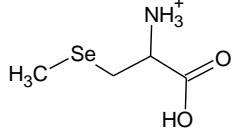


6	20.8	ND	268.08103	268.08101	-0.1	$C_{10}H_{20}NO_2Se$	+	$C_5H_7O_2$	99.04
								$C_6H_{10}O_2$	114.07
								$C_8H_{16}NO_2$	158.12
								$C_9H_{19}NO_2$	173.14
								$C_7H_{13}O_2Se$	209.00



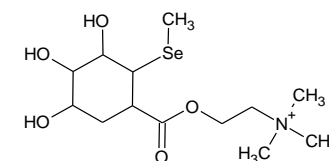
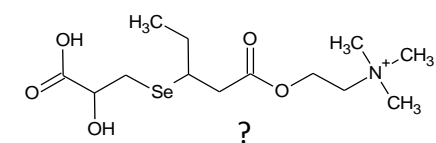
7	24.7	29.2	240.04973	240.04985	0.5	$C_8H_{18}NO_2Se$	+	C_2H_5Se	108.96
								C_3H_5OSe	136.95
								$C_5H_9O_2Se$	180.98



8	30.7	22.5	180.98756	180.98754	-0.1	C₄H₉N₂OSe	+	C ₃ H ₅ Se C ₃ H ₆ NSe C ₃ H ₇ OSe C ₄ H ₇ N ₂ Se	120.96 135.97 138.97 162.98	Se-allyl-N-hydroxy-selenourea 
9	32.8	13.6	198.00278	198.00286	0.4	C₅H₁₂NO₂Se	+	/	/	Selenomethionine (Table 1) 
9b	32.8	13.6	195.98713	195.98733	1.0	C ₅ H ₁₀ NO ₂ Se	+	/	/	Oxidized selenomethionine 
10	34.7	5.5	408.07674	408.07698	0.6	C₁₂H₂₆NO₉Se	+	/	/	Methylseleno-Se-deoxypentose-hexose 
11	34.8	4.6	183.98713	183.98732	1.0	C₄H₁₀NO₂Se	+	/	/	Methylselenocysteine 

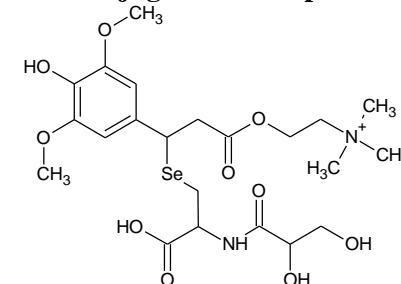
12	37.9	28.2	356.09714	356.09718	0.1	C ₁₃ H ₂₆ NO ₅ Se	+	C ₇ H ₁₁ O ₂	127.08
								C ₃ H ₇ Se	134.97
								C ₃ H ₅ O ₂ Se	152.95
								C ₅ H ₇ O ₂ Se	178.96
								C ₇ H ₁₁ O ₂ Se	206.99
								C ₆ H ₁₁ O ₃ Se	210.99
								C ₇ H ₁₃ O ₃ Se	225.00
								C ₉ H ₁₅ O ₂ Se	235.02
								C ₁₀ H ₂₂ NO ₂ Se	268.08
								C ₁₀ H ₁₇ O ₅ Se	297.02

Selenized choline ester



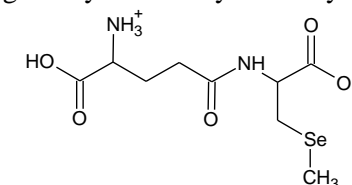
13	39	28.3	567.14587	567.14587	0.0	C ₂₂ H ₃₅ N ₂ O ₁₀ Se	+	C ₄ H ₇ O ₂	87.04
								C ₆ H ₁₁ O ₃	167.07
								C ₆ H ₁₀ NO ₅	176.06
								C ₁₁ H ₁₁ O ₄	207.07
								C ₆ H ₁₀ NO ₄ Se	239.98
								C ₉ H ₁₁ O ₃ Se	246.99
								C ₁₃ H ₁₅ O ₅	251.09
								C ₆ H ₁₀ NO ₅ Se	255.97
								C ₁₆ H ₂₅ NO ₅	311.17
								C ₁₂ H ₁₆ NO ₅ Se	334.02
C ₁₆ H ₂₆ NO ₅ Se	392.10								
C ₁₅ H ₂₀ NO ₈ Se	422.03								

N-2,3-dihydroxypropionyl-selenocysteine conjugated to sinapine



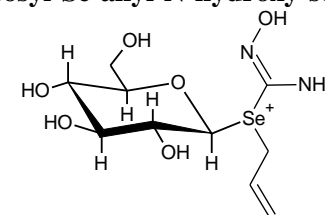
14	40.6	8.5	313.02976	313.02953	-0.7	C ₉ H ₁₇ N ₂ O ₅ Se	+	/	/
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γ-glutamyl-Se-methylselenocysteine

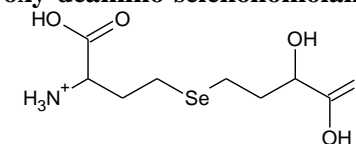


15	41.2	16.5	343.04029	343.04023	-0.2	$C_{10}H_{19}N_2O_6Se$	+	$C_4H_5O_2$	85.03
								$C_5H_5O_2$	97.03
								C_3H_5Se	120.96
								$C_6H_7O_3$	127.04
								C_3H_6NSe	135.97
								C_3H_7OSe	138.97
								$C_6H_9O_9$	145.05
								$C_4H_7N_2Se$	162.98
								$C_4H_9N_2OSe$	180.99
								16	41.3
$C_4H_5O_2$	85.03								
$C_4H_8NO_2$	102.05								
C_3H_5Se	120.96								
C_4H_5OSe	148.95								
$C_4H_7O_2Se$	166.96								
$C_4H_{10}NO_2Se$	183.99								
$C_6H_{12}NOSe$	194.01								
$C_7H_{14}NO_3Se$	240.01								
17	41.4	ND	346.00362	346.00374	0.3	$C_9H_{16}NO_8Se$	+	$C_3H_8NO_3$	106.04
								$C_3H_5O_3Se$	168.94
								$C_6H_{10}NO_5$	176.06
								$C_5H_7O_3Se$	194.96
								$C_5H_{10}NO_3Se$	211.98
								$C_6H_9O_5Se$	240.96
								$C_6H_{10}NO_5Se$	255.97

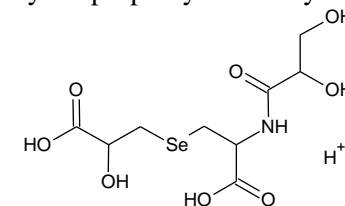
Se-glucosyl-Se-allyl-N-hydroxy-selenourea



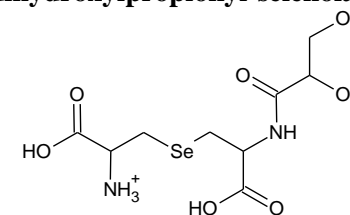
Hydroxy-deamino-selenohomolanthionine



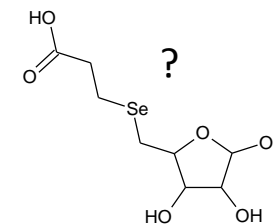
2-hydroxy-3-selenylpropanoic acid-N-2,3-dihydro-propionyl-selenocysteine



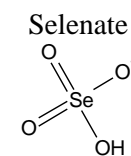
18 43.9 2.9 345.01969 345.01929 -1.2 C₉H₁₇N₂O₇Se + / / N-2,3-dihydroxypropionyl-selenolanthionine



19 45.1 2.3 304.02939 304.02917 -0.7 C₈H₁₈NO₆Se + C₂H₅Se 108.96
 C₄H₅Se 132.95
 C₃H₅OSe 136.95
 C₅H₅OSe 160.95
 C₅H₇O₂Se 178.96
 C₅H₉O₃Se 196.97
 C₅H₁₁O₄Se 214.98
 5'-3-selenylpropanoic acid-ribofuranose ?
 NH₄⁺

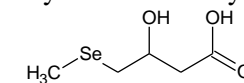


20 ND 29 144.90455 144.90452 -0.2 HSeO₄ - / /



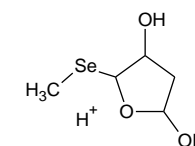
21 ND 21 198.98679 198.98686 0.4 $C_5H_{11}O_3Se$ + $C_4H_7O_2$ 87.04

Methylseleno carbohydrate



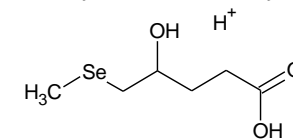
H^+

or

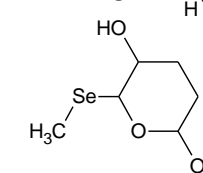


22 ND 21.3 213.00244 213.00238 -0.3 $C_6H_{13}O_3Se$ + $C_4H_7O_2$ 87.04
 $C_5H_9O_2$ 101.06

Methylseleno carbohydrate

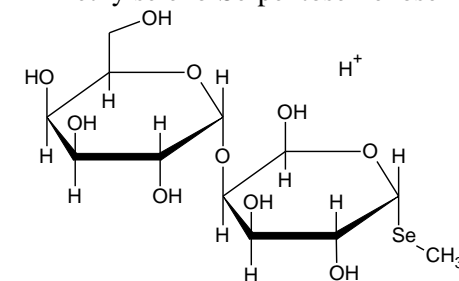


or



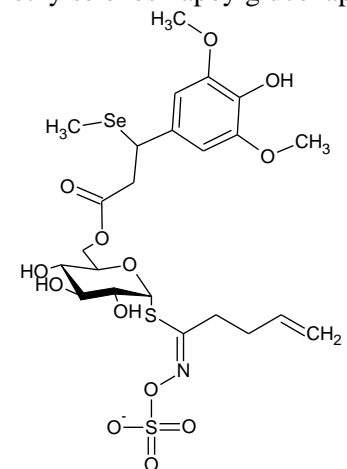
23 ND 1.7 407.04546 407.04474 -1.8 $C_{12}H_{23}O_{10}Se$ + / /

Methylseleno-Se-pentose-hexose



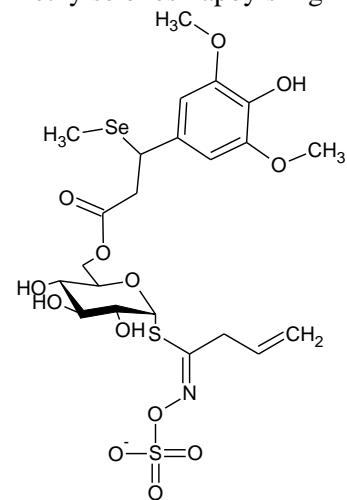
24 7.8 / 674.04795 674.04864 -1.0 C₂₃H₃₂NO₁₃S₂Se - /^d /^d

Methylselenosinapoylgluconapin

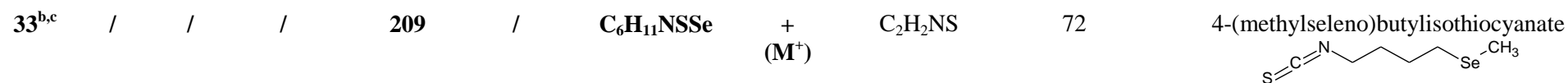


25 9.3 / 660.03303 660.03298 0.1 C₂₂H₃₀NO₁₃S₂Se - /^d /^d

Methylselenosinapoylsinigrin



28	13.5	/	573.01304	573.01213	1.6	$C_{18}H_{25}N_2O_{10}S_2Se$	-	/ ^d	/ ^d	Methylselenoneoglucobrassicin or methylseleno-4-methoxyglucobrassicin
29 ^{a,b}	/	/	RT matching	/	/	$C_2H_6Se_2$	/	/	/	Dimethyldiselenide $H_3C-Se-Se-CH_3$
30 ^{b,c}	/	/	/	163	/	C_5H_9NSe	+ (M ⁺)	C_2H_5Se	109/107	4-(methylseleno)butanenitrile
31 ^{b,c}	/	/	/	177	/	$C_6H_{11}NSe$	+ (M ⁺)	C_2H_5Se	109/107	5-(methylseleno)pentanenitrile
32 ^{b,c}	/	/	/	195	/	$C_5H_9N_2S_2Se$	+ (M ⁺)	C_2H_2NS	72	3-(methylseleno)propylisothiocyanate



^a Dimethyldiselenide was identified by retention time matching with the corresponding standard. ^b Compounds **29** to **33** were observed by GC ICP MS and GC APCI TQ MS coupling (low resolution) ^c Compounds **30** to **33** were identified through their specific mass transitions. ^d These Se glucosinolates are present at trace levels and their identification was done according to the determine structure of the closely eluting abundant analogue forms lacking the methylselenol group. Methylselenol group was predicted to react with the available oxidative-sensitive double bond present in these species.