

Supplementary Material

Green and white asparagus (*Asparagus officinalis*): A Source of Developmental, Chemical and Urinary Intrigue

Eirini Pegiou ¹, Roland Mumm ², Parag Acharya ³, Ric C.H. de Vos ², Robert D. Hall ^{1,2,4,*}

¹ Wageningen University & Research, Laboratory of Plant Physiology, P.O. Box 16, 6700AA Wageningen, The Netherlands; eirini.pegiou@wur.nl

² Wageningen University & Research, Business Unit Bioscience, P.O. Box 16, 6700AA Wageningen, The Netherlands; roland.mumm@wur.nl (R.M.); ric.devos@wur.nl (R.C.H.d.V.)

³ Unilever Foods Innovation Centre, Bronland 14, 6708WH Wageningen, The Netherlands; parag.acharya@unilever.com

⁴ Netherlands metabolomics Centre, Einsteinweg 55, 2333CC Leiden, The Netherlands

* Correspondence: robert.hall@wur.nl

Supplementary Tables

Table S1: List of non-volatile secondary metabolites detected and reported in *A. officinalis* (green and/or white) materials (when not indicated, this was not reported in the article and green can be assumed). For the description of the analytical techniques the following codes apply; the separation or ionization technique (HPLC: high performance liquid chromatography, MALDI: matrix assisted laser desorption/ionization) and the detector (MS: mass spectrometry, UV: ultraviolet, NMR: nuclear magnetic resonance, I: imaging) (MW: molecular weight in g/mol, FW: fresh weight, DW: dry weight).

<i>Detected secondary metabolite, Molecular formula (MW)</i>	<i>Asparagus material (reported concentration)</i>	<i>Analytical technique (Reference)</i>
Polyphenols		
<i>Flavonoids</i>		
quercetin-3-O-rutinoside (rutin), $C_{27}H_{30}O_{16}$ (610.5)	Green spears (2.28 mg/100 g FW and 0.05 % FW in top section) [1]	HPLC-MS [1–4]
	Green spears (ca. 7 mg/g DW in top section, 5 mg/g DW in middle section, 2 mg/g DW in bottom sections)	HPLC-UV at 210 nm [5]
	White spears (<0.5 mg/g DW)	HPLC-UV at 210 nm [5]
	White spears (1.1 mg/100 g FW) & green spears (48.2 mg/100 g FW)	HPLC-MS [6]
	Cooked white spears	HPLC-MS [7]

	Asparagus waste	HPLC-UV & MS [8]
	Green spears	HPLC-MS [9] and HPLC-MS/MS & MALDI-IMS [10]
apigenin-6-8-di-C-glucoside (vicenin 2), <i>C</i> ₂₇ <i>H</i> ₃₀ <i>O</i> ₁₅ (549.5)	Green spears	HPLC-MS [9]
apigenin rhamnoside, <i>C</i> ₂₁ <i>H</i> ₂₀ <i>O</i> ₉ (416.4)		HPLC-MS [3]
quercetin-3-O-glucosyl-rutinoside, <i>C</i> ₃₃ <i>H</i> ₄₀ <i>O</i> ₂₁ (772.7)		HPLC-MS [9]
quercetin-3-β-D glucoside, <i>C</i> ₂₁ <i>H</i> ₁₉ <i>O</i> ₁₂ (463.4)		HPLC-MS [3,9]
quercetin diglucoside, <i>C</i> ₂₇ <i>H</i> ₃₀ <i>O</i> ₁₇ (626.5)		HPLC-MS [9]
quercetin triglycoside, <i>C</i> ₃₃ <i>H</i> ₄₀ <i>O</i> ₂₂ (788.7)		HPLC-MS [4]
quercetin galactoside, <i>C</i> ₂₁ <i>H</i> ₂₀ <i>O</i> ₁₂ (464.38)		HPLC-MS [3]
isorhamnetin-3-O-rutinoside, <i>C</i> ₂₈ <i>H</i> ₃₂ <i>O</i> ₁₆ (624.5)		HPLC-MS [3]
isorhamnetin-3-O-rutinoside (narcissin), <i>C</i> ₂₈ <i>H</i> ₃₂ <i>O</i> ₁₆ (624.5)		HPLC-MS [4,9]
noricaritin-O-glucoside (amurensin), <i>C</i> ₂₆ <i>H</i> ₃₀ <i>O</i> ₁₂ (534.5)		HPLC-MS [9]
kaempferol-3-O-rutinoside (nicotiflorin), <i>C</i> ₂₇ <i>H</i> ₃₀ <i>O</i> ₁₅ (594.5)		HPLC-MS [4,9]
kaempferol glucoside, <i>C</i> ₂₁ <i>H</i> ₂₀ <i>O</i> ₁₁ (448.4)	Green spears Asparagus waste	HPLC-MS [3,9] HPLC-UV & MS [8]
kaempferol-O-acetylglucoside, <i>C</i> ₂₃ <i>H</i> ₂₂ <i>O</i> ₁₂ (490.4)	Green spears	HPLC-MS [9]
kaempferol-3-p-coumaroyl-glucoside,		

$C_{30}H_{26}O_{13}$ (594.52)		
quercetin,	Green spears (0.14 mg/100 g FW)	HPLC-MS [2,9]
$C_{15}H_{10}O_7$ (302.24)	Asparagus waste	HPLC-UV & MS [8]
<i>Phenolic acids</i>		
ferulic acid,	Green spears (1.05 mg/100 g FW)	HPLC-MS [2,3,9]
$C_{10}H_{10}O_4$ (194.18)	Asparagus waste	HPLC-UV & MS [8]
	Cooked white spears	HPLC-MS [7]
vanillic acid,	Green spears	HPLC-MS [9]
$C_8H_8O_4$ (168.15)		
3-caffeoylquinic acid (chlorogenic acid),		HPLC-MS [3,9]
$C_{16}H_{18}O_9$ (354.31)		
3-p-coumaroylquinic acid,		HPLC-MS [3,9]
$C_{16}H_{18}O_8$ (338.31)		
5-caffeoylquinic acid (neochlorogenic acid)/1-caffeoylquinic acid,		
$C_{16}H_{18}O_9$ (354.31)		
<i>Saponins</i>		
protodioscin,	Asparagus seeds	¹ H- & ¹³ C-NMR [11]
$C_{51}H_{84}O_{22}$ (1049.2)		
	Asparagus spears (0.24 mg/100 g FW in top section, 25mg/100 g FW in bottom section)	HPLC-MS [1]
	Green spears (<1 mg/g DW)	HPLC-UV at 210 nm [5]
	White spears (ca 2.6 mg/g DW in top section, 3.7 mg/g DW in middle section, 4-5 mg/g DW in bottom section)	
	White spears (0.66-13.6 mg/100 g) & green spears (0.3 mg/100 g)	HPLC-MS/MS [12]
dioscin,	White spears (6.18-33.9 mg/100 g) & green spears (6.49 mg/100 g)	HPLC-MS/MS [12]
$C_{45}H_{72}O_{16}$ (869.05)		
methyl protodioscin,	Green spears (0.65 mg/100 g)	
$C_{52}H_{86}O_{22}$ (1063.2)		
asparasaponin (ASP) I,	White spears (0.32-3.75 mg/100 g) & green spears (0.3 mg/100 g)	
$C_{51}H_{84}O_{22}$ (1049.2)		

asparasaponin II, $C_{45}H_{74}O_{18}$ (903.1) (25R/S)-dihydro-ASP-II	White spears (0.02-0.4 mg/100 g) & green spears (0.1 mg/100 g)	
yamogenin, $C_{27}H_{42}O_3$ (414.6)	White spears (bottom parts) Green spears	HPLC-UV at 210 nm [13] HPLC-MS and 1H & 13C NMR [14]
sarsasapogenin, $C_{27}H_{44}O_3$ (416.6)	Asparagus roots	HPLC-MS and 1H & 13C NMR [15]
Sulphur compounds		
asparagusic acid, $C_4H_6O_2S_2$ (150.2)	White spears (10.6 mg/100 g FW) & green spears (9.86 mg/100 g FW) Green spears	HPLC-MS [6,9] HPLC-MS [9]
asparaptine, $C_{10}H_{18}N_4O_3S_2$ (306.4)	White spears (29.8 mg/100 g FW) & green spears (25.1 mg/100 g FW) Green spears	HPLC-MS [6] HPLC-MS/MS & MALDI-IMS [16]
Other compounds		
(1 stilbene, 2 lignans, 36 oxylipins, 2 glyceroglycolipids and 4 others)	Green spears	HPLC-MS [9]

Table S2: List of volatile secondary metabolites detected and reported in *A. officinalis* (green and/or white) materials (when not indicated, this was not reported in the article and green can be assumed). For the description of the analytical techniques the following codes apply; the trapping or extraction technique (SPE: liquid solid phase extraction, LLE: liquid liquid extraction, SDE: simultaneous steam distillation extraction, SPME: solid phase microextraction, TDU: thermal desorption), separation (GC: gas chromatography) and the detector (MS: mass spectrometry, O: olfactometry). (MW: molecular weight in g/mol). **key odorants based on the literature reported in this review and summarized in Table 2.

<i>Detected secondary metabolites, Molecular formula (MW)</i>	<i>Asparagus material (reported concentration in ppb)</i>	<i>Analytical technique (Reference)</i>
Alcohols		
n-butanol, $C_4H_{10}O$ (74.12)	Cooked white spears (160)	SPE-GC-MS [17]

1-penten-3-ol, <i>C5H10O</i> (86.13)	Cooked white spears (80)	
2-penten-1-ol, <i>C5H10O</i> (86.13)	Cooked white spears (100)	
1-pentanol, <i>C5H12O</i> (88.15)	Cooked white spears (2300)	
	Cooked white spears	SDE-GC-MS [7,18–20]
2-pentanol, <i>C5H12O</i> (88.15)	Cooked white spears (25)	SPE-GC-MS [17]
2,4-hexadien-1-ol, <i>C6H10O</i> (98.145)	Cooked white spears (20)	
2-hexen-1-ol, <i>C6H12O</i> (100.16)	Cooked white spears (240)	
1-hexanol, <i>C6H14O</i> (102.162)	Cooked white spears (8400)	
	Cooked white spears	SDE-GC-MS [7,18,19]
2,4-heptadien-1-ol, <i>C7H12O</i> (112.17)	Cooked white spears (65)	SPE-GC-MS [17]
2-hepten-1-ol, <i>C7H14O</i> (114.186)	Cooked white spears (300)	
1-heptanol, <i>C7H16O</i> (116.88)	Cooked white spears (25)	
benzyl alcohol, <i>C7H8O</i> (108.14)	Cooked white spears (410)	
2-phenylethanol, <i>C8H10O</i> (122.16)	Cooked white spears (440)	
3-methyl-1-butanol, <i>C5H12O</i> (88.148)	Cooked white spears (80)	
1-octen-3-ol **, <i>C8H16O</i> (128.21)	Green asparagus juice (42.8)	SPME-GC-MS [21]
	Cooked white spears (300)	SPE-GC-MS [17]
	Cooked white spears	SDE-GC-MS [19,20]
	Asparagus spears	TDU-GC-MS [22]
2-octen-1-ol, <i>C8H16O</i> (128.21)	Cooked white spears (300)	SPE-GC-MS [17]
1-octanol, <i>C8H18O</i> (130.23)	Cooked white spears (70)	

2,4-nonadien-1-ol, <i>C9H16O</i> (140.22)	Cooked white spears (50)	
2-nonen-1-ol, <i>C9H18O</i> (142.24)	Cooked white spears (20)	
1-nonanol, <i>C9H20O</i> (144.26)	Green asparagus juice (1)	SPME-GC-MS [21]
	Cooked white spears (60)	SPE-GC-MS [17]
2,4-decadien-1-ol, <i>C10H18O</i> (154.249)	Cooked white spears (70)	
Aldehydes		
2-butenal, <i>C4H6O</i> (70.09)	Green asparagus juice (25.5)	SPME-GC-MS [21]
	Cooked white spears	SDE-GC-MS [18–20]
3-methyl-butanal, <i>C5H10O</i> (86.13)	Green asparagus juice (4.4)	SPME-GC-MS [21]
pentanal, <i>C5H10O</i> (86.13)	Green asparagus juice (51.3)	SPME-GC-MS [21]
	Cooked white spears	SPE-GC-MS [17] and SDE-GC-MS [19,20]
2-methyl-2-butenal, <i>C5H8O</i> (84.12)	Green asparagus juice (31.3)	SPME-GC-MS [21]
2-pentenal, <i>C5H8O</i> (84.12)	Green asparagus juice (18.2)	
2-methyl-2-pentenal, <i>C6H10O</i> (98.14)	Green asparagus juice (0.8)	
2-hexenal **, <i>C6H10O</i> (98.14)	Green asparagus juice (13.2)	
	Cooked white spears	SPE-GC-MS [17] and SDE-GC-MS [18–20]
	Asparagus spears	TDU-GC-MS [22]
hexanal **, <i>C6H12O</i> (100.16)	Green asparagus juice (259.2)	SPME-GC-MS [21]
	White spears (100)	SPE-GC-MS [17]
	Cooked white spears	SDE-GC-MS & GCO [7,19,20]

	Asparagus spears	TDU-GC-MS [22]
2,4-heptadienal, <i>C7H10O</i> (110.15)	Green asparagus juice (2)	SPME-GC-MS [21]
2-heptenal, <i>C7H12O</i> (112.17)	Green asparagus juice (52.7)	
	White spears (30)	SPE-GC-MS [17]
	Cooked white spears	SDE-GC-MS [7,19,20]
heptanal, <i>C7H14O</i> (114.188)	Green asparagus juice (1)	SPME-GC-MS [21]
benzaldehyde, <i>C7H6O</i> (106.12)	Green asparagus juice (0.9)	SPME-GC-MS [21]
	Cooked white spears	SPE-GC-MS [17] and SDE-GC-MS [7]
2,4-octadienal, <i>C8H12O</i> (124.18)	Green asparagus juice (1.6)	SPME-GC-MS [21]
2-octenal, <i>C8H14O</i> (126.2)	Green asparagus juice (17.5)	
	Cooked white spears	SPE-GC-MS [17] and SDE-GC-MS [19,20]
octanal, <i>C8H16O</i> (128.212)	Green asparagus juice (1.7)	SPME-GC-MS [21]
phenylacetaldehyde, <i>C8H8O</i> (120.15)	Cooked white spears	SDE-GC-MS [18–20]
2,4-nonadienal, <i>C9H14O</i> (138.21)		
2-nonenal, <i>C9H16O</i> (140.226)	Cooked white spears (10)	SPE-GC-MS [17]
nonanal, <i>C9H18O</i> (142.239)	Green asparagus juice (3.4)	SPME-GC-MS [21]
2-phenyl-2-butenal, <i>C10H10O</i> (149.19)	Cooked white spears (10)	SPE-GC-MS [17]
2,4-decadienal, <i>C10H16O</i> (152.23)	Green asparagus juice (1.1)	SPME-GC-MS [21]
	Cooked white spears	SPE-GC-MS [17] and SDE-GC-MS [7,19,20]

2-dodecenal, <i>C₁₂H₂₂O</i> (182.3)	Green asparagus juice (1.1)	SPME-GC-MS [21]
Ketones		
2,3-butanedione **, <i>C₄H₆O₂</i> (86.09)	Cooked white spears	SDE-GC-MS [7,18–20]
3-hydroxy-2-butanone, <i>C₄H₈O₂</i> (88.11)	Cooked white spears (6400)	SPE-GC-MS [17]
3-hydroxy-2-pentanone, <i>C₅H₁₂O₂</i> (102.13)	Cooked white spears (80)	
2,3-pentanedione **, <i>C₅H₈O₂</i> (100.12)	Cooked white spears	SDE-GC-MS & GCO [7,18–20]
2-hexanone, <i>C₆H₁₂O</i> (100.161)	Cooked white spears (10)	SPE-GC-MS [17]
2,5-cyclohexadienone, <i>C₆H₆O</i> (94.11)	Cooked white spears (90)	
2-heptanone, <i>C₇H₁₄O</i> (114.18)	Cooked white spears (15)	
3,5-octadien-2-one, <i>C₈H₁₂O</i> (124.18)	Green asparagus juice (3.9)	SPME-GC-MS [21]
3,5-octadien-2-one, <i>C₈H₁₂O</i> (124.18)	Cooked white spears (70)	SPE-GC-MS [17]
1-octen-3-one, <i>C₈H₁₄O</i> (126.2)	Green asparagus juice (22.5)	SPME-GC-MS [21]
6-methyl-5-hepten-2-one, <i>C₈H₁₄O</i> (126.2)	Green asparagus juice (1.5)	
3-octen-2-one, <i>C₈H₁₄O</i> (126.2)	Green asparagus juice (0.7)	
3-octen-2-one, <i>C₈H₁₄O</i> (126.2)	Cooked white spears (10)	SPE-GC-MS [17]
2,3-octanedione **, <i>C₈H₁₄O₂</i> (142.2)	Cooked white spears	SDE-GC-MS & GCO [18–20]
3-octanone, <i>C₈H₁₆O</i> (128.21)	Green asparagus juice (2.3)	SPME-GC-MS [21]
3,5-nonadien-2-one, <i>C₉H₁₄O</i> (138.207)	Cooked white spears (10)	SPE-GC-MS [17]
3,5-decadien-2-one, <i>C₁₀H₁₆O</i> (152.23)	Cooked white spears (10)	
β-ionone, <i>C₁₃H₂₀O</i> (192.3)	Green asparagus juice (1.4)	SPME-GC-MS [21]

geranyl acetone, <i>C13H22O</i> (194.31)	Green asparagus juice (0.3)	
Esters		
ethyl dodecanoate, <i>C14H28O2</i> (228.37)	Green asparagus juice (0.7)	SPME-GC-MS [21]
diisobutyl phthalate, <i>C16H22O4</i> (278.34)	Green asparagus juice (1.9)	
ethyl hexadecanoate, <i>C18H36O2</i> (284.5)	Green asparagus juice (0.6)	
Carboxylic acids		
3-methylbutanoic acid, <i>C5H10O2</i> (102.13)	Green asparagus juice (1)	SPME-GC-MS [21]
pentanoic acid, <i>C5H10O2</i> (102.13)	Green asparagus juice (0.6)	
hexanoic acid, <i>C6H12O2</i> (116.158)	Green asparagus juice (2.1)	
Pyrazines		
2-methylpyrazine, <i>C5H6N2</i> (94.11)	Cooked white spears	SDE-GC-MS [7,19,20]
2-ethylpyrazine, <i>C6H8N2</i> (108.14)	White spears	SPE-GC-MS [17]
2,5-dimethylpyrazine, <i>C6H8N2</i> (108.14)	White spears (35)	
	Cooked white spears	SDE-GC-MS [19,20]
2,6-dimethylpyrazine **, <i>C6H8N2</i> (108.14)	White spears (200)	SPE-GC-MS [17]
	Cooked white spears	SDE-GC-MS & GCO [7,19,20]
2,3-dimethylpyrazine, <i>C6H8N2</i> (108.14)	White spears	SPE-GC-MS [17]
2-ethyl-6-methylpyrazine, <i>C7H10N2</i> (122.17)		
2-ethyl-5-methylpyrazine, <i>C7H10N2</i> (122.17)		
2-ethyl-3,5-dimethyl pyrazine **, <i>C8H12N2</i> (136.19)	Cooked white spears	SDE-GC-MS & GCO [19,20]
2-methoxy-3-isopropyl pyrazine **, <i>C8H12N2O</i> (152.19)		

2-isobutyl-3-methoxypyrazine **, <i>C9H14N2O</i> (152.19)	Cooked white spears	SPE-GC-MS [17] & SDE-GC-MS [20]
Furans		
2-ethyl-furan, <i>C6H8O</i> (96.13)	Green asparagus juice (0.2)	SPME-GC-MS [21]
	Cooked white spears	SPE-GC-MS [17]
	Cooked white spears	SDE-GC-MS [19,20]
2-pentyl-furan **, <i>C9H14O</i> (138.21)	Green asparagus juice (2.3)	SPME-GC-MS [21]
	Cooked white spears (165)	SPE-GC-MS [17]
	Cooked white spears	SDE-GC-MS [7,19,20]
	Asparagus spears	TDU-GC-MS [22]
Sulphur compounds		
dimethyl sulfone, <i>C2H6O2S</i> (94.13)	Cooked white spears (30)	SPE-GC-MS [17]
dimethyl sulfoxide, <i>C2H6OS</i> (78.13)	Cooked white spears	SDE-GC-MS [19,20]
dimethyl sulfide **, <i>C2H6S</i> (62.14)	Cooked white spears (3300)	SPE-GC-MS [17]
	Cooked white spears	SDE-GC-MS [19,20]
S-methyl thioacetate, <i>C3H6OS</i> (90.15)	Cooked white spears	SDE-GC-MS & GCO [19,20]
3-methylthiopropanol, <i>C4H10OS</i> (106.19)	Cooked white spears (10)	SPE-GC-MS [17]
methyl propyl sulfide, <i>C4H10S</i> (90.19)	Cooked white spears	SDE-GC-MS [18,19]
3-methylthio-propanal **, <i>C4H8OS</i> (104.17)		SPE-GC-MS & GCO [17] SDE-GC-MS [7,19,20]
thiophene-2-carbaldehyde, <i>C5H4OS</i> (112.15)	Cooked white spears (10)	SPE-GC-MS [17]
2-acetylthiazole, <i>C5H5NOS</i> (127.17)	Cooked white spears (10)	
	Cooked white spears	SDE-GC-MS [19,20]

2-hydroxymethylthiophene, <i>C5H6OS</i> (114.17)	Cooked white spears (20)	SPE-GC-MS [17]
methyl-1,2-dithiolane-4- carboxylate, <i>C5H8O2S2</i> (164.28)	Cooked white spears (7000)	
ethyl-1,2-dithiolane-4- carboxylate, <i>C6H10O2S2</i> (178.27)	Cooked white spears (50)	
2-formyl-3-methylthiophene, <i>C6H6OS</i> (126.18)	Cooked white spears (70)	
3-vinyl-3,4-dihydro-1,2-dithiine, <i>C6H8S2</i> (144.26)	Cooked white spears (20)	
Other compounds		
methoxy-phenyl-oxime, <i>C8H9NO2</i> (151.16)	Green asparagus juice (18.9)	SPME-GC-MS [21]
2,4-di-tert-amylphenol, <i>C16H26O</i> (234.38)	Green asparagus juice (4.3)	

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