

**Table S1.** Multiple reaction monitoring (MRM) settings for the analysis of melanin pyrolysate by GC/MS/MS.

Time segment	Retention time [min]	Compound (Type <sup>b</sup> )	MS transition		Collision Energy [V]
			Precursor Ion [m/z]	Product Ion [m/z]	
1	9.6	Thiazole (P)	85	58	15
			58	57	12
	10.8	Toluene (NS)	92	91	15
			91	65	16
2	15.7	Styrene (NS)	104	77	27
			104	78	15
			103	77	14
3	19.1	Phenol (NS)	94	65	26
	21.4–22.0	Methylphenol <sup>a</sup> (NS)	94	66	16
			108	107	16
			107	77	16
4	24.9	1,2-Benzenediol (NS)	110	63	30
			110	64	20
			110	92	15
	25.3	Benzothiazole (P)	135	108	18
			108	82	12
5	26.5	Indole (NS)	117	89	30
			117	90	16
			90	63	27
6	27.7	4-Hydroxybenzothiazole (P)	151	96	23
			151	123	12
			123	96	10
	28.1	Methylindole (NS)	130	77	27
			130	103	14
			103	77	10
7	28.8–29.4	2,3-Dihydro-5H-1,4-benzothiazin-5-one <sup>a</sup> (P)	165	110	18
			165	136	22
			136	109	16
8	30.3–30.6	7-Methyl-2,3-dihydro-5H-1,4-benzothiazin-5-one <sup>a</sup> (P)	179	110	15
			179	150	20
			178	109	20
	30.5–30.9	4-Hydroxy-6-ethylbenzothiazole <sup>a</sup> (P)	179	164	15
			164	109	20
			164	136	15
9	31.4	7-Methyl-5H-1,4-benzothiazin-5-one (P)	177	121	30
			177	148	20
			148	77	27

<sup>a</sup> Isomers. <sup>b</sup> P – pheomelanin marker, NS – non-sulfur-containing pyrolysis product.

The two distinct groups of products were monitored in each pyrolysate: heterocyclic compounds with 1,3-thiazole or 1,4 thiazine rings, which are characteristic of thermally degraded pheomelanin (the pheomelanin markers, P) and the products devoid of sulfur (NS). The latter group of compounds are always formed in high yields during the pyrolysis of melanin, irrespective of its structural type and origin, and therefore we use them for normalization of pyrolysis data.