Supplemental materials

Methyl syringate mono-glucoside is a crucial intermediate in leptosperin biosynthesis in *Leptospermum scoparium* (manuka)

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Table S-1. Positive MRM^{HR} combinations and data extraction setting of TOF/MS

Compounds (Name)	Mode	Adduct /Charge	Precursor ion	Fragment ion	DP [a]	CE [b]
MSYR_1	MRM^{HR}	$[M+H]^+$	213.1	181.0507	80	16
MSYR_2	MRM^{HR}	$[M+H]^+$	213.1	154.0638	80	20
MSYR-d_6_1	MRM^{HR}	$[M+H]^+$	219.1	169.0454	80	30
MSYR-d_6 _2	MRM^{HR}	$[M+H]^+$	219.1	141.0516	80	20
Leptosperin_1	MRM^{HR}	$[M+NH_4]^+$	554.1	213.0761	40	45
Leptosperin_2	MRM^{HR}	$[M+NH_4]^+$	554.1	181.0497	40	50
Leptosperin_3	MRM^{HR}	$[M+NH_4]^+$	554.1	154.0638	40	50
Leptosperin-d_6_1	MRM^{HR}	$[M+NH_4]^+$	560.2	325.1143	40	10
Leptosperin-d_6_2	MRM^{HR}	$[M+NH_4]^+$	560.2	219.1145	40	10
Leptosperin-d_6_3	MRM^{HR}	$[M+NH_4]^+$	560.2	187.0883	40	50
MSYR-Glc_1	MRM^{HR}	$[M+NH_4]^+$	392.1	213.0769	80	15
MSYR-Glc_2	MRM^{HR}	$[M+NH_4]^+$	392.1	181.0506	80	35
MSYR-Glc-d_6_1	MRM^{HR}	$[M+NH_4]^+$	398.1	219.1143	80	15
MSYR-Glc-d_6_2	MRM^{HR}	$[M+NH_4]^+$	398.1	187.0883	80	35
Forchlorfenuron [c]_1	MRM^{HR}	$[M+H]^+$	248.0	129.0224	80	25
Forchlorfenuron [c]_2	MRM^{HR}	$[M+H]^+$	248.0	93.0460	80	35
MSYR-TOF	TOF	$[M+H]^+$	213.07575	–	80	5
MSYR-d_6-TOF	TOF	$[M+H]^+$	219.11341	–	80	5
Leptosperin-TOF	TOF	$[M+NH_4]^+$	554.20795	–	80	5
Leptosperin-d_6-TOF	TOF	$[M+NH_4]^+$	560.24561	–	80	5
MSYR-Glc-TOF	TOF	$[M+NH_4]^+$	392.15512	–	80	5
MSYR-d_6-Glc-TOF	TOF	$[M+NH_4]^+$	398.19278	–	80	5
Forchlorfenuron [c]-TOF	TOF	$[M+H]^+$	248.05852	–	80	5

[a] DP, declustering potential. [b] CE, collision energy. [c] Forchlorfenuron is used as an internal standard.

Table S-2. Negative MRM^{HR} combinations and data extraction settings of TOF/MS

Compounds (Name)	Mode	Adduct /Charge	Precursor ion	Fragment ion	DP [a]	CE [b]
MSYR_1	MRM^{HR}	$[M-H]^-$	211.0	196.0376	-75	-20
MSYR_2	MRM^{HR}	$[M-H]^-$	211.0	181.0156	-75	-25
MSYR-d_6_1	MRM^{HR}	$[M-H]^-$	217.1	199.8503	-75	-25
MSYR-d_6_2	MRM^{HR}	$[M-H]^-$	217.1	181.0140	-75	-25
Leptosperin_1	MRM^{HR}	$[M+FA-H]^-$	581.2	211.0608	-25	-35
Leptosperin_2	MRM^{HR}	$[M+FA-H]^-$	581.2	323.0984	-25	-15
Leptosperin-d_6_1	MRM^{HR}	$[M+FA-H]^-$	587.2	217.0986	-25	-35
Leptosperin-d_6_2	MRM^{HR}	$[M+FA-H]^-$	587.2	323.0983	-25	-15
MSYR-Glc_1	MRM^{HR}	$[M+FA-H]^-$	419.1	211.0611	-25	-25
MSYR-Glc_2	MRM^{HR}	$[M+FA-H]^-$	419.1	196.0377	-25	-40
MSYR-d_6-Glc_1	MRM^{HR}	$[M+FA-H]^-$	425.1	217.0990	-25	-25
MSYR-d_6-Glc_2	MRM^{HR}	$[M+FA-H]^-$	425.1	181.0140	-25	-40
Forchlorfenuron [c]_1	MRM^{HR}	$[M-H]^-$	246.0	91.0303	-30	-40
Forchlorfenuron [c]_2	MRM^{HR}	$[M-H]^-$	246.0	127.0071	-30	-18
MSYR-TOF	TOF	$[M-H]^-$	213.07575	–	-80	-15
MSYR-d_6-TOF	TOF	$[M-H]^-$	219.11341	–	-80	-15
Leptosperin-TOF	TOF	$[M+FA-H]^-$	581.17232	–	-80	-15
Leptosperin-d_6-TOF	TOF	$[M+FA-H]^-$	587.20998	–	-80	-15
MSYR-Glc-TOF	TOF	$[M+FA-H]^-$	419.11950	–	-80	-15
MSYR-Glc-d_6-TOF	TOF	$[M+FA-H]^-$	425.15716	–	-80	-15
Forchlorfenuron [c]-TOF	TOF	$[M-H]^-$	248.05852	–	-80	-15

[a] DP, declustering potential. [b] CE, collision energy. [c] Forchlorfenuron is used as an internal standard.

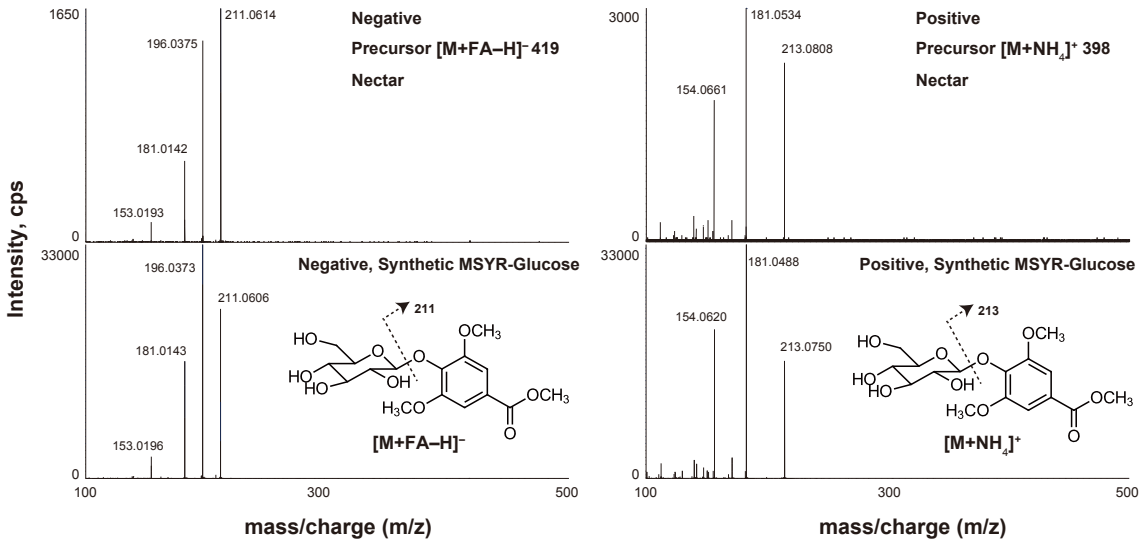

Figure S1. Mass identification of methyl syringate (MSYR)-glucose from nectar. The collision-induced fragmentation of MSYR-glucose from nectar and synthetic MSYR-glucose (STD) was examined by UHPLC-Q-TOF/MS with positive and negative ionization. The molecular structure of MSYR-glucose with possible fragmentation is shown in the figure inset.