Supporting Information

Simultaneous determination of six glycosidic aroma precursors in pomelo by ultra high-performance liquid chromatography-tadem mass spectrometry

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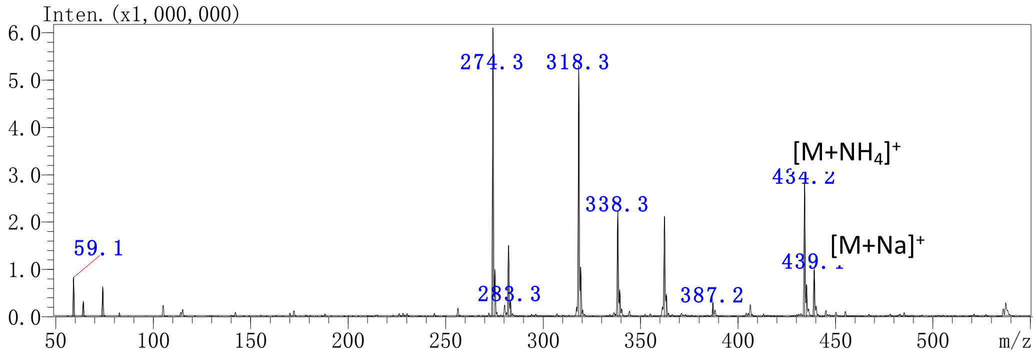

Fig.S1. The spectrum of 2-phenylethyl β-primeveroside in 5 mmol ammonium acetate by positive ESI scan.

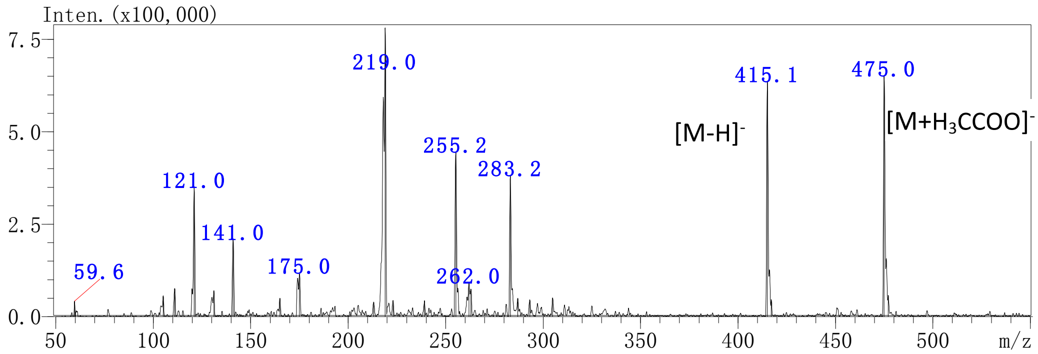

Fig. S2. The Spectrum of 2-phenylethyl β-primeveroside in 5 mmol ammonium acetate by negative ESI scan.

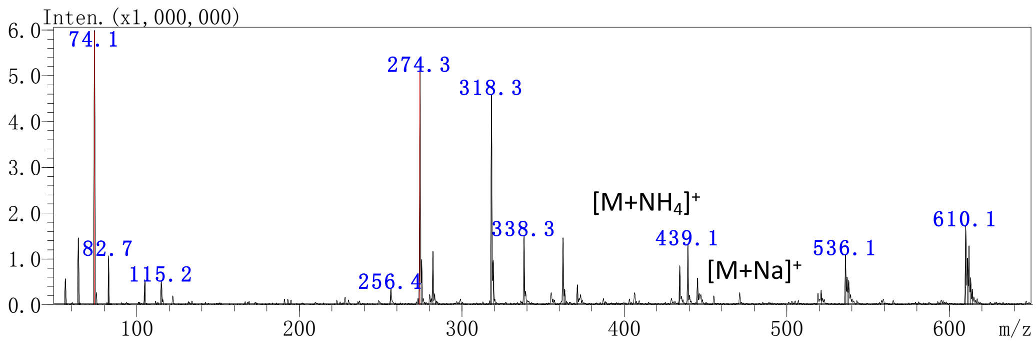

Fig. S3. The spectrum of 2-phenylethyl β-primeveroside in 0.1% formic acid by positive ESI scan.

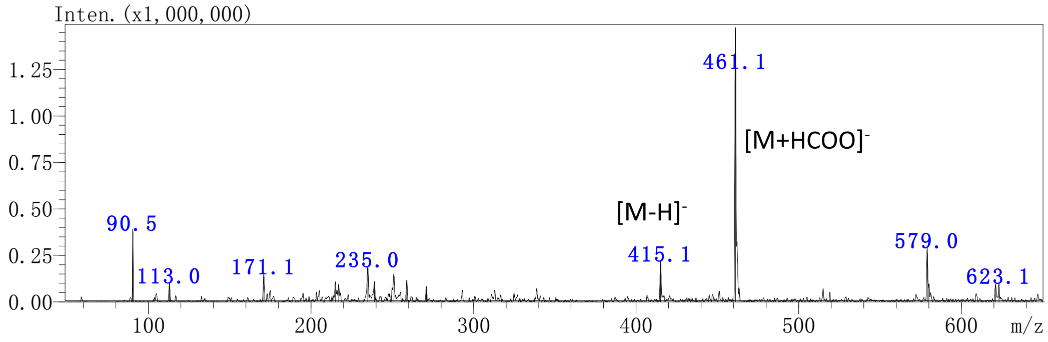

Fig. S4. The spectrum of 2-phenylethyl β-primeveroside in 0.1% formic acid by negative ESI scan.

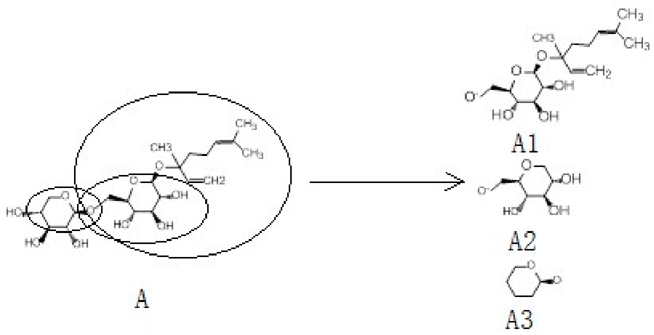

Fig. S5. The MS/MS fragmentation pathways of linalool β-primeveroside: A) The structure of linalool β-primeveroside, MW: 448.2 Da; A1) The product ion, MW: 315.1 Da; A2) The product ion, MW: 161.0 Da; A3) The product ion, MW: 101.0 Da.

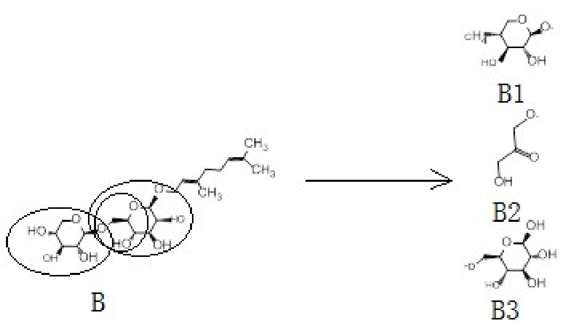

Fig. S6. The MS/MS fragmentation pathways of geraniol β-primeveroside: B) The structure of geraniol β-primeveroside, MW:448.2 Da; B1) The product ion, MW:149.0 Da; B2. The product ion, MW:89.0 Da; B3) The product ion, MW:178.9 Da.

Table S1. Main adduct ions of glycosidic aroma precursors ESI source scan in positive or negative ion mode

Analyte	Molecular weight	5 mmol/L ammonia acetate		0.1% formic acid	
		Positive ESI scan	Negative ESI scan	Positive ESI scan	Negative ESI scan
Geraniol β-glucoside	316.2	-	375.1[b]	-	361.1[e]
Geraniol β-primeveroside	448.2	466.2[a]	507.1[b],447.1[c]	*471.2*[d]	493.1[e]
Linalool β-primeveroside	448.2	466.2[a]	507.1[b],447.1[c]	471.2[d]	493.1[e]
Benzyl β-primeveroside	402.2	420.2[a]	401.1[b],461.1[c]	425.1[d]	447.0[e]
2-phenylethyl β-primeveroside	416.2	434.2[a]	475.0[b],415.1[c]	439.1[d]	461.1[e]
Nerolidol β-primeveroside	516.3	534.3[a]	575.2[b],515.2[c]	539.2[d]	561.1[e]

Indication: [a] adduct ion: $[M+NH_4]^+$, [b] adduct ion: $[M+H_3CCOO]^-$, [c] adduct ion: $[M-H]^-$, [d] adduct ion: $[M+Na]^+$,[e] adduct ion: $[M+HCOO]^-$.

Table S2. Six glycosidic aroma precursors profile in leaves, flowers and fruits of pomelo plant (n=3)

	Geraniol β-glucoside (μg/kg)	Geraniol β-primeveroside (μg/kg)	Linalool β-primeveroside (μg/kg)	Benzyl β-primeveroside (μg/kg)	2-phenylethyl β-primeveroside (μg/kg)	Nerolidol β-primeveroside (μg/kg)
Flowers of pomelo	470.8±20.1	1252.9±39.6	65.0±2.1	241.3±5.3	30.8±1.1	134.2±5.7
Leaves of pomelo	-	-	45.5±1.4	5964.9±130.0	502.2±9.2	-
Fruits of pomelo	-	-	18.0±0.9	614.8±23.8	93.7±4.4	-

Indication: [a] no detecation, and LOD of Geraniol β-glucoside, Geraniol β-primeveroside and Nerolidol β-primeveroside are 4.47 ng/mL, 2.23 ng/mL and 0.321 ng/mL, individually.

Table S3. The extraction coefficients of glycosidic aroma precursors with different solvent (n=3)

Analytes	Spiking(μg/kg)[a]	Recovery (%)[b]		
		Acetonitrile	Water	Methanol
Geraniol β-glucoside	595.2	84.0±2.5	65.7±2.2	96.6±0.8
Geraniol β-primeveroside	297.0	75.8±2.4	79.5±2.1	105.3±1.4
Linalool β-primeveroside	104.5	60.3±2.9	95.6±0.9	95.5±1.3
Benzyl β-primeveroside	265.6	76.6±6.0	102.0±3.4	95.3±0.7
2-Phenylethyl β-primeveroside	106.2	68.8±1.8	89.2±0.8	95.2±1.7
Nerolidol β-primeveroside	42.7	69.7±1.8	50.5±3.2	94.8±1.4

Indication: [a] the standard mixtures of glycosidic aroma precursors was spiked into 2 gram fruit of pomelo, [b] percentage recovery of glycosidic aroma precursors in fruit of pomelo expressed as mean±SD.

Table S4. The extraction coefficients of glycosidic aroma precursors with different approches (n=3)

Analytes	Spiking (μg/kg)[a]	Recovery (%)[b]		
		Homogenization	Ultrasonic bath	Combination approches[c]
Geraniol β-glucoside	595.2	87.5±1.4	90.2±1.3	102.6±3.8
Geraniol β-primeveroside	297.0	92.2±2.4	89.5±0.8	105.7±2.9
Linalool β-primeveroside	104.5	84.1±1.2	90.9±1.7	105.2±1.9
Benzyl β-primeveroside	265.6	86.8±3.1	88.4±2.4	96.8±2.7
2-phenylethyl β-primeveroside	106.2	91.3±2.1	88.4±3.2	105.3±1.3
Nerolidol β-primeveroside	42.7	89.5±1.2	93.9±2.1	98.7±2.5

Indication: [a] the standard mixtures of glycosidic aroma precursors was spiked into 2 gram fruit of pomelo; b percentage recovery of glycosidic aroma precursors in fruit of pomelo expressed as mean±SD， and the extraction solvent was methanol; [c] The combination approaches was as follow: samples in methanol were homogenized for 2 min at 10000 rpm, and then extracted in ultrasonic bath for 20 min.