

Supplementary information

Spatial distribution mapping of molecules in the grains of different rice landraces, using desorption electrospray ionization mass spectrometry

Arunan Suganya¹, Debal Deb², and Thalappil Pradeep^{1*}

¹ DST Unit of Nanoscience, and Thematic Unit of Excellence, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

² Centre for Interdisciplinary Studies, Barrackpore 700 123, India

*Corresponding author: Thalappil Pradeep

Tel: +91-44-2257 4208, E-mail: pradeep@iitm.ac.in

Table of contents:

Particulars	Title	Page No.
Table S1	Morphological characteristics of the rice landraces examined	2
Figure S1	DESI MS spectrum from resin and grain surface	2
Figure S2	DESI MS imaging using different concentrations of methanol	3
Figure S3	SEM and EDAX characterization of H24 rice whole grain section	4
Figure S4	Tandem MS data of representative molecular ions using ESI MS and DESI MS	5
Figure S5	Metabolite chart of molecule identified in positive ion mode DESI MSI	6
Figure S6	Product ion MS/MS of unidentified molecules	7

Rice landrace	Code	Phenol reaction	Grain aroma	Grain pericarp colour
Garib-sal	G02	Strong	Absent	White
Gouri sundari	G28	Strong	Strong	Dark brown
Gazepxali	G38	Absent	Strong	White
Huggi bhatta	H24	Strong	Strong	Dark purple
Hendebaihar	H34	Absent	Absent	Light brown
Kataribhog	K11	Strong	Mild	White
Kala Nuniya	K86	Strong	Strong	White
Radha Tilak	R09	Absent	Mild	White
Tikki	T05	Strong	Absent	Black
Tike Churi	T11	Weak	Absent	Dark brown

Table S1. Morphological Characteristics of the Rice Landraces Examined.

Rice fragrance is tested olfactorily, by a group of people, who report the strength of aroma they perceive. Phenol reaction was tested by soaking the rice seeds in 2% phenol for 6 hours, when the rice hull colour becomes dark (strong reaction), light purple (weak) or remains unchanged (no reaction).

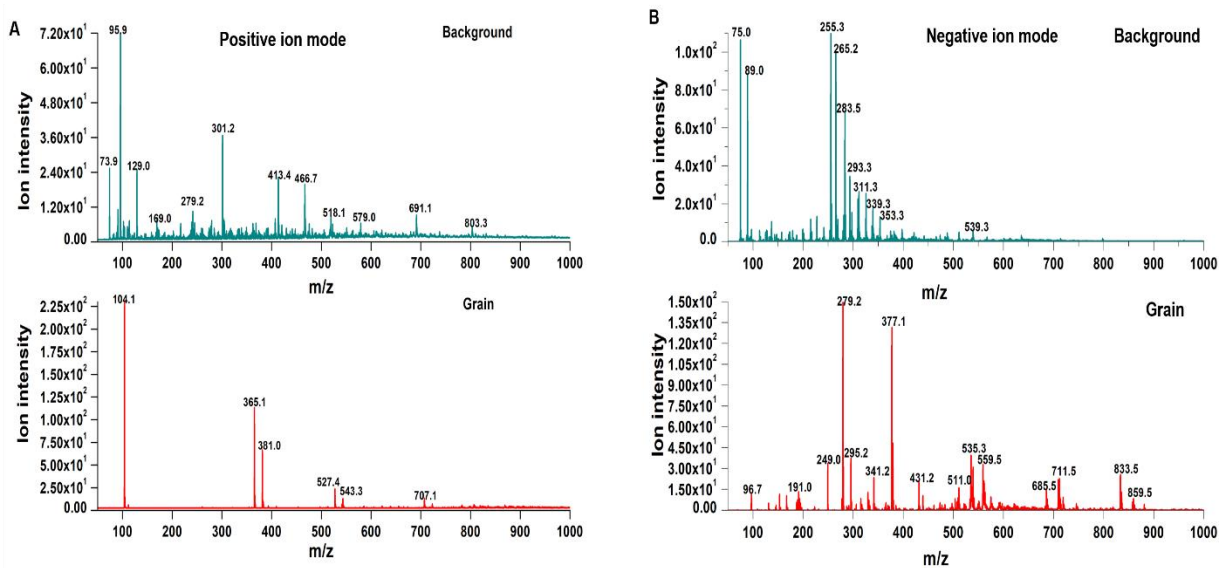


Figure S1: DESI MS spectra collected from the background and grain surface of H24 rice in the A) positive, and B) negative ion mode.

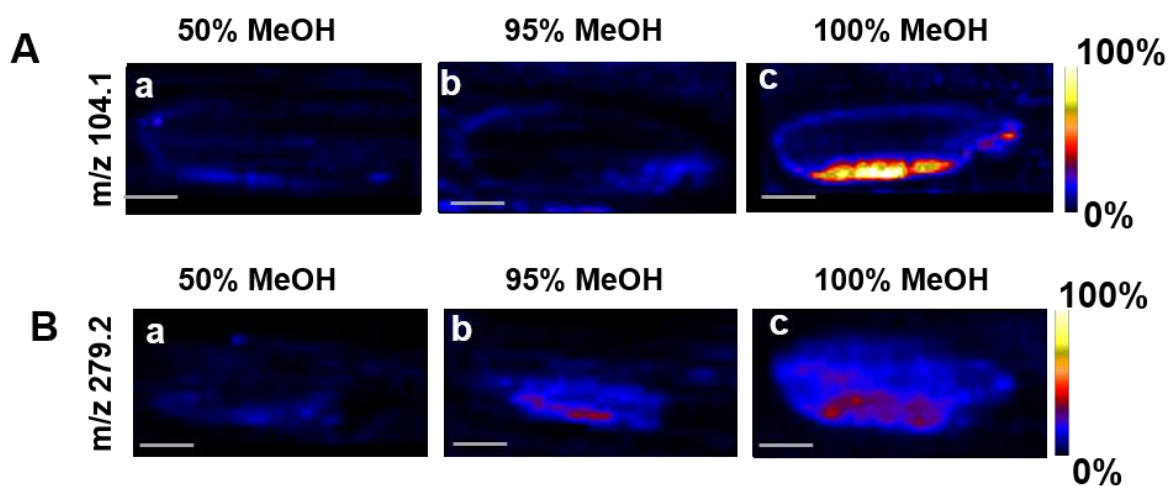


Figure S2: DESI MS imaging of H24 rice using different concentrations of methanol as spray solvent. A & B) molecular ion image of choline and linoleic acid obtained from positive and negative ion mode imaging, respectively. a) 50% MeOH, b) 95% MeOH and c) 100% MeOH.

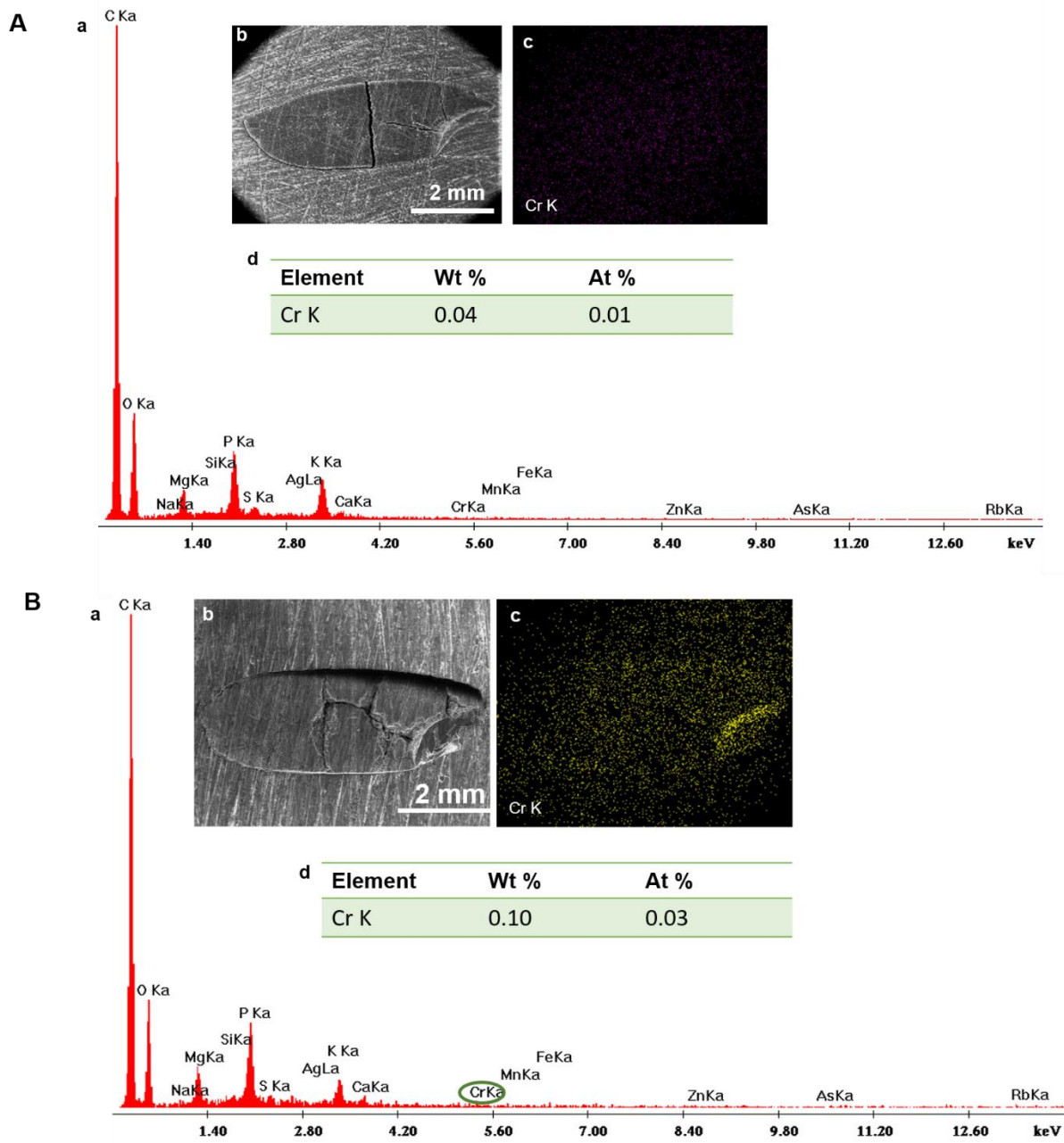


Figure S3: SEM-EDAX mapping of G2 rice A) Control, and B) treated with chromium (Cr^{3+}) metal ion solution. In both A & B, a) EDAX spectrum, b) SEM image of G2 rice, c) EDAX image and e) elemental ratio of chromium.

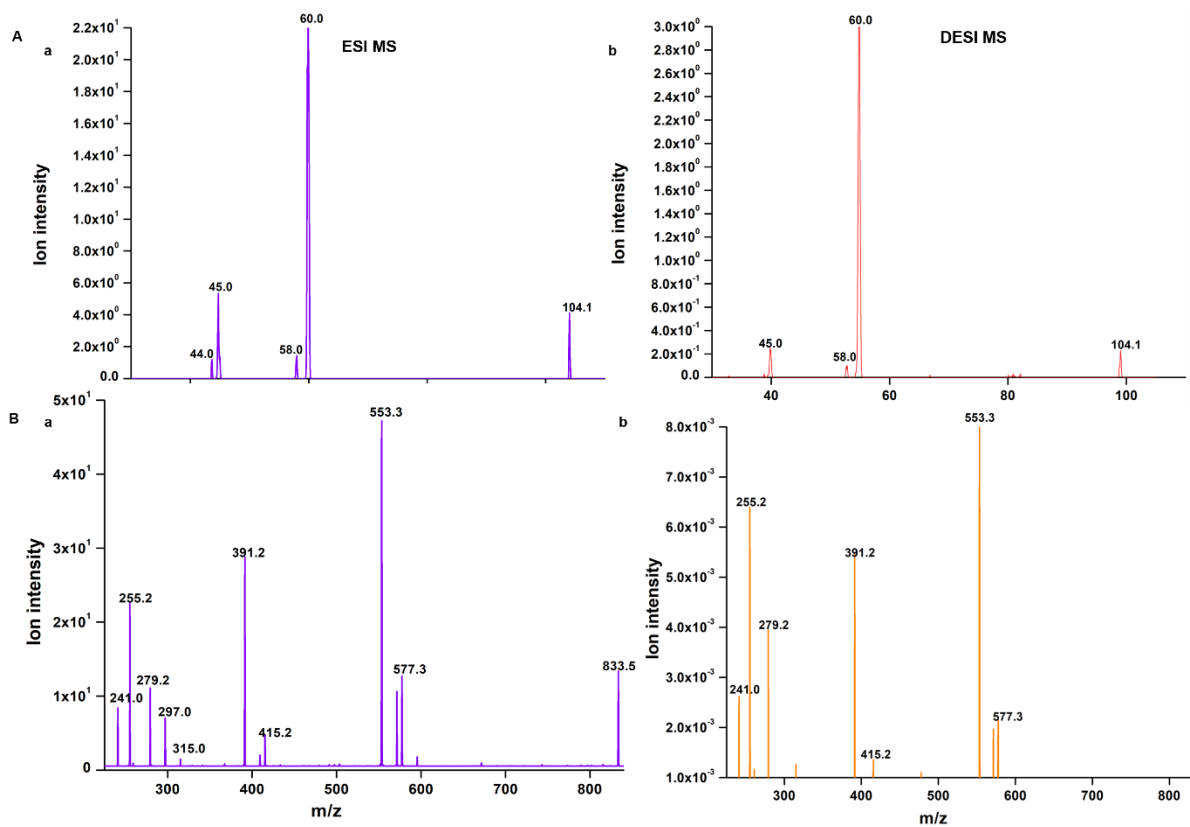


Figure S4: Tandem MS/MS data of A) choline and B) PI (34:2) in positive and negative ion mode, respectively using a) ESI MS and b) DESI MS.

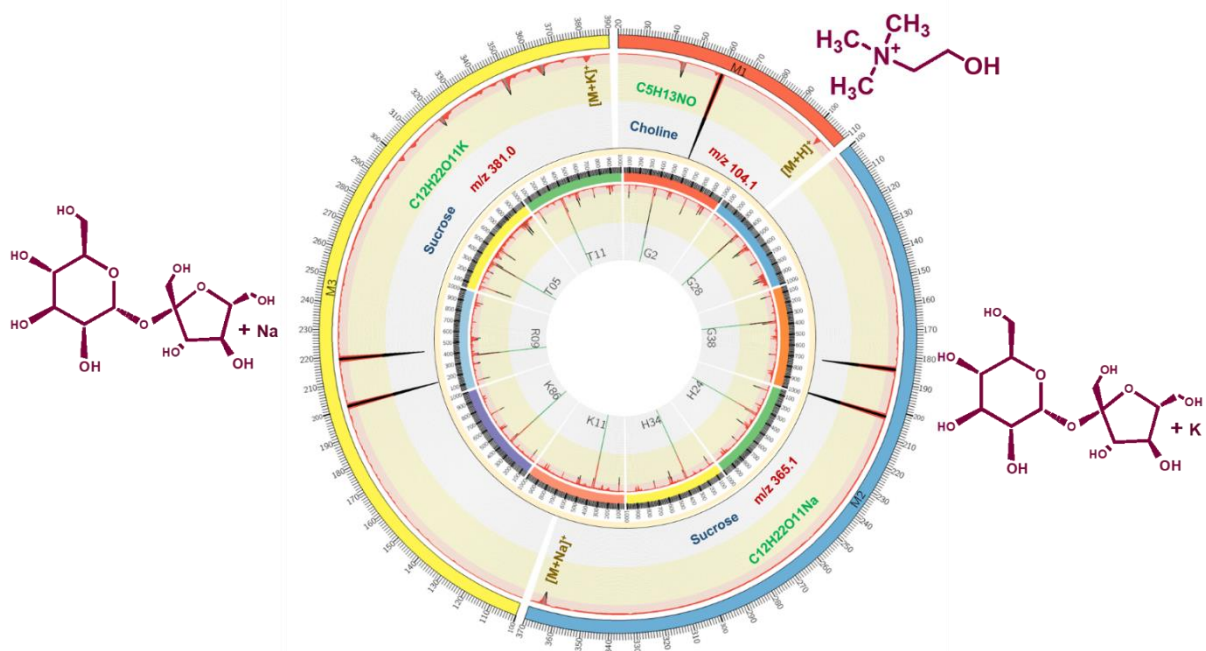
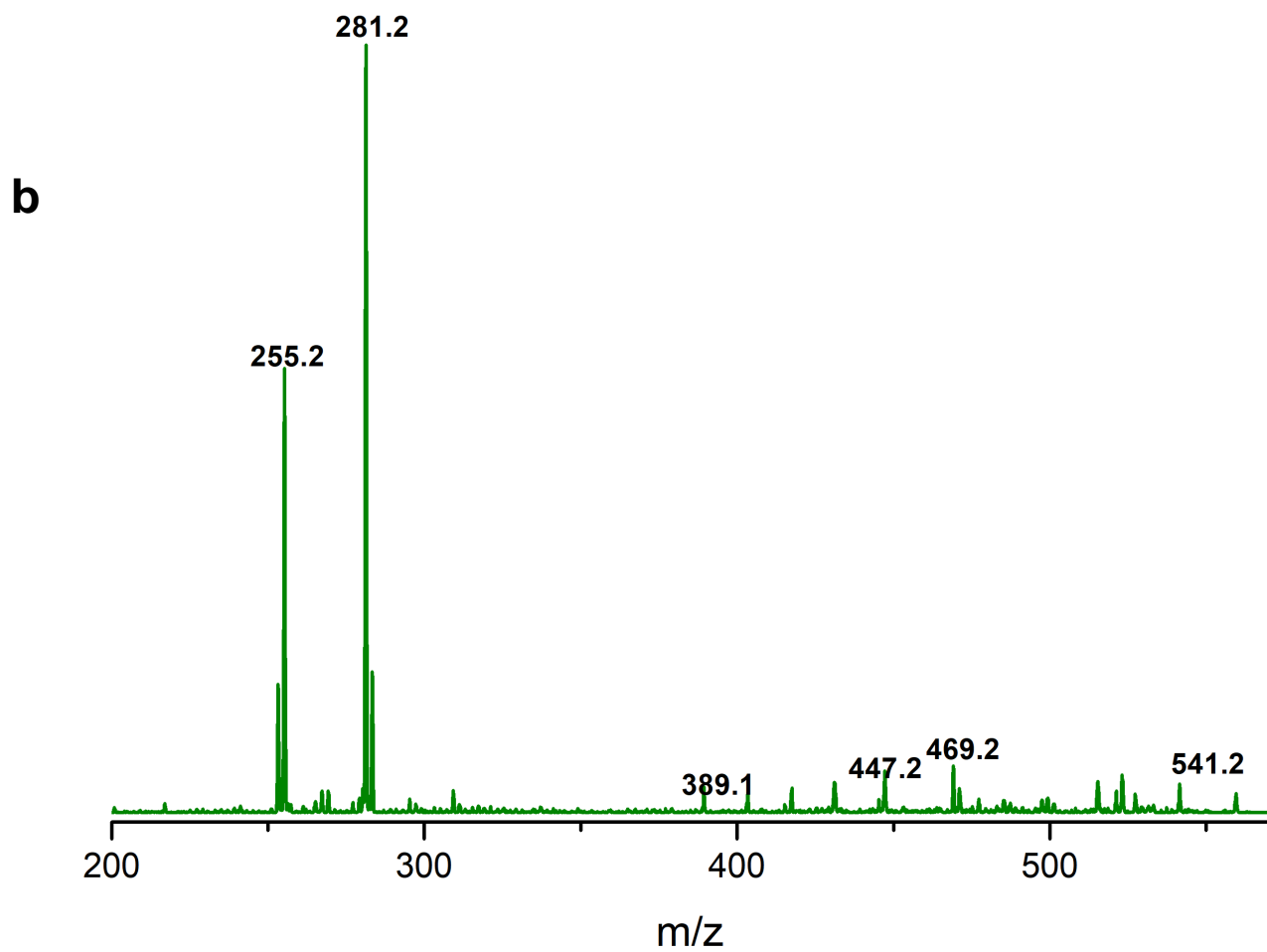
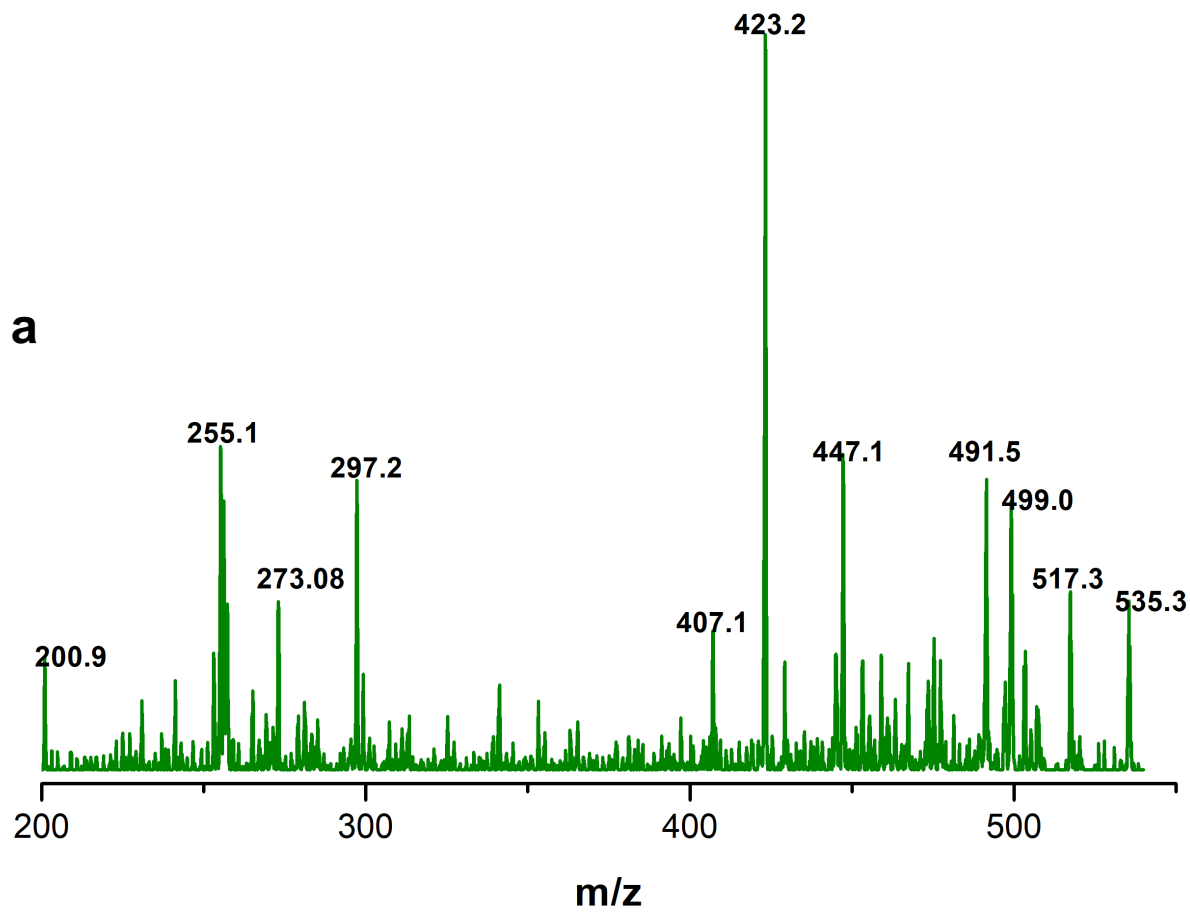


Figure S5: The metabolite chart representing the MS, MS/MS, and chemical information data from the ESI MS analysis of the rice grain extracts of various landraces corresponding to the molecules identified by DESI MS imaging, in positive ion mode. Inner circle represents MS data and the outer circle denotes the tandem MS data.

In the positive ionization mode, protonated choline (m/z 104.1, $[C_5H_{14}NO]^+$) was identified by its characteristic fragment ions at m/z 60.1 $[(CH_3)_3NH]^+$, and m/z 45.1 $[C_2H_5O]^+$ as a result of H_2C-N bond cleavage. The disaccharide, sucrose was identified from its characteristic CID spectrum. The glycosidic cleavage produced fragment ions at m/z 203.0 and 185.0 from sodiated sucrose and m/z 219.0 and 201.0 from potassiated sucrose ion. The fragments at m/z 203.0 and 219.0 and m/z 185.0 and 201.0 correspond to the neutral loss of 162 and 180 mass units from their molecular ion peaks, respectively. The identified molecules were further confirmed by comparison with the mass spectrum from the METLIN database (Choline, id: 56; sucrose, id: 137).



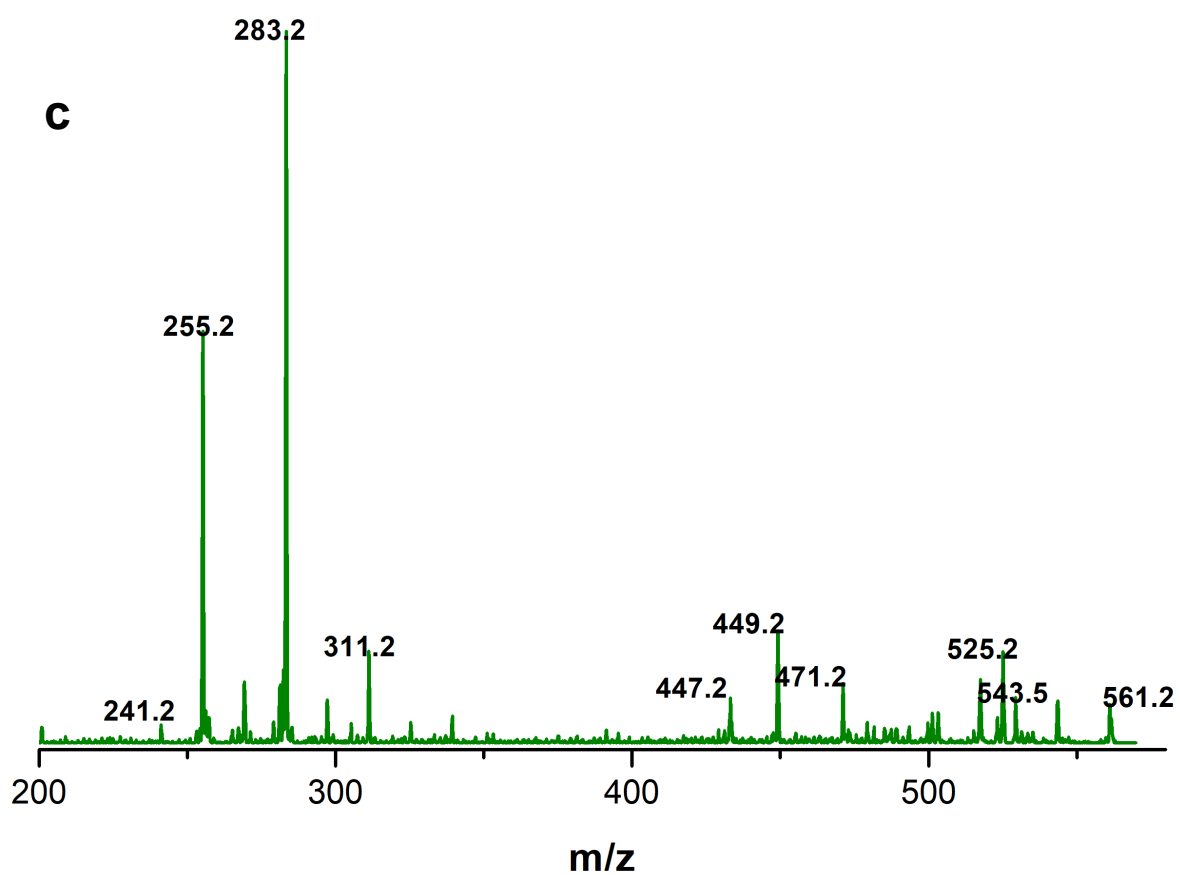


Figure S6. The product ion MS/MS data of unidentified molecules a) 535, b) 559 c)561