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Title: **Metabotyping of 30 maize hybrids under early-sowing conditions reveals potential marker metabolites for breeding**

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Supplementary Table S2: Table of chemical shifts used for identification and quantification of metabolites in ^{1}H-NMR spectra of polar extracts (in deuterated phosphate buffer solution, apparent pH 6.0) of maize leaf, expressed as relative values to the TSP resonance at 0 ppm. s: singlet, d: doublet, bd: broad doublet, dd: doublet of doublets, t: triplet, td: triplet of doublets, m: multiplet.

Compounds	Assignment	^{1}H Chemical shift (ppm)	^{1}H Pattern	Use (quantification or detection)	MSI status [a]
Alanine	β-CH_3	1.487	d	q	1
Betaine	N-CH_3	3.27	s	q	1
Chlorogenate1 (hydroxycinnamic-containing compound)	=CH	6.42	d	q	3
	CH_{arom}	6.93	d	d	
	CH_{arom}	7.12	dd	d	
	CH_{arom}	7.19	d	d	
	=CH	7.63	d	d	
Chlorogenate2 (hydroxycinnamic and quinic-containing compound)	=CH	6.36	d	q	2
	CH_{arom}	6.98	d	d	
	CH_{arom}	7.09	dd	d	
	CH_{arom}	7.16	d	d	
	=CH	7.62	d	d	
	quinic H5	5.32	m	d	
	quinic H?	4.25	m	d	
Choline	N-CH_3	3.2	s	q	1
	N-CH_2	3.53	m	d	
Citrate	CH_2	2.7	d	q	1
	CH_2	2.55	d	d	
Fructose		4.12	m	q	1
Glucose	α-CH	5.24	d	q	1
	β-CH	4.65	d	q	1
Glutamate	γ-CH_2	2.36	td	q	1
Glycine	α-CH	3.56	s	q	1
Inositol	C_5H	3.29	t	q	1
Isoleucine	δ-CH_3	0.94	t	d	1
	γ´-CH_3	1.01	d	q	
Leucine	δ-CH_3	0.96	d	d	1
	δ´-CH_3	0.97	d	d	1
Malate	α-CH	4.31	dd	q	1
	β-CH	2.68	dd	d	
	β´-CH	2.39	dd	d	
Putrescine	CH_2	1.77	m	q	1

Putrescine	$N\text{-}CH_2$	3.06	m	d	
Quinate1		1.93	dd	q	3
Quinate2 (probably free quinic acid)		1.88	dd	q	3
		1.96	m	d	
		1.98	m	d	
		2.04	d	d	
		2.07	m	d	
		4.03	m	d	
		4.15	dd	d	
Raffinose		4.99	d	q	2
Rhamnose		5.12	d	q	1
		1.3	d	d	
		1.28	d	d	
Shikimate		4.04	dd	q	1
		2.79	bd	d	
		2.75	bd	d	
Succinate	CH_2	2.42	s	q	1
Sucrose		5.42	d	q	1
		4.22	d	d	
		4.06	t	d	
		3.9	m	d	
		3.82	m	d	
		3.77	t	d	
		3.68	s	d	
		3.57	dd	d	
		3.48	t	d	
Trans-aconitate	=CH	6.62	s	q	1
	CH_2	3.47	s	d	
Trigonelline	=CH-N	9.12	s	q	1
	CH-C=C-N	8.84	m	d	
	CH=C-N	8.09	t	d	
	CH_3	4.45	s	d	
Valine	$\gamma'\text{-}CH_3$	0.99	d	q	1
Unknown compounds					
UnkD0.65		0.65	d	q	4
UnkD0.68		0.68	d	q	4
UnkD1.44		1.44	d	q	4
UnkM2.91		2.91	m	q	4
UnkM5.39		5.39	m	q	4

[a] Identification status according to MSI (Sumner *et al.* , 2007): 1, Identified compounds (checked with standard); 2, Putatively annotated compounds; 3, Putatively characterized compound classes; 4, Unknown.