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ORIGINAL ARTICLE

Diversity and association of phenotypic and metabolomic traits in the close model grasses *Brachypodium distachyon*, *B. stacei* and *B. hybridum*

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Running Title: Phenotypic and metabolomic study of annual *Brachypodium* species

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Background and Aims Morphological traits in combination with metabolite fingerprinting were used to investigate inter and intra species diversity within the model annual grasses *B. distachyon*, *B. stacei* and *B. hybridum*.

Methods Phenotypic variation of 15 morphological characters and 2219 nominal mass (*m/z)* signals generated using Flow Infusion Electrospray ionisation - Mass Spectrometry (FIE-MS) were evaluated in individuals from 174 wild populations and 6 inbred lines and 12 lines of the three species, respectively. Basic statistics and multivariate Principal Component Analysis (PCA) and Discriminant Analysis (DA) were used to differentiate inter- and intraspecific variability of the two types of variables, and their association was assayed with *rcorr*.

Key results Basic statistics and ANOVA detected eight phenotypic characters [(stomata) leaf guard cell length, pollen grain length, (plant) height, second leaf width, inflorescence length, number of spikelets per inflorescence, lemma length, awn length] and 434 tentatively annotated metabolite signals that significantly discriminated the three species. Three phenotypic traits (pollen grain length, spikelet length, number of flowers per inflorescence) might be genetically fixed. The three species showed different metabolomic profiles. DA significantly discriminated the three taxa with both, morphometric and metabolome traits and the intraspecific phenotypic diversity within *B. distachyon* and *B. stacei*. The populations of *B. hybridum* were considerably less differentiated.

Conclusions Highly explanatory metabolite signals together with morphological characters revealed concordant patterns of differentiation of the three taxa. Intraspecific phenotypic diversity was observed between northern and southern Iberian populations of *B. distachyon* and between E Mediterranean – SW Asian and W Mediterranean populations of *B. stacei*. Significant association was found for pollen grain length and lemma length and 10 and 6 metabolomic signals, respectively. These results would guide the selection of new germplasm lines of the three model grasses in on-going GWAS experiments.

Key words: association studies, *Brachypodium distachyon*, *Brachypodium stacei*, *Brachypodium hybridum*, metabolite fingerprinting, phenotypic traits, statistic analyses

INTRODUCTION

Wild plants and, to a lesser extent, cultivated crop species exhibit large phenotypic and metabolomic diversity as a consequence of their individuals' responses to developmental growth conditions and adaptation to environmental factors (Fiehn, 2002). Characterization of phenotypic and metabolomic traits, and their biological dynamics, have become a major line of research in the new era of 'omics' features (Fiehn, 2001, Fiehn, 2002, Hall et al., 2002), due to their importance for Genome-Wide-Association-Studies (GWAS; Matsuda et al., 2015). Thus, phenomic and high resolution metabolomic approaches have been used in conjunction with genomic, transcriptomic and proteomic data to detect and map genes, regulatory sequences and epigenomic regulators in the genomes, and to unravel the plastic and biochemical variation of individuals under different intrinsic and extrinsic scenarios. Phenotypic and metabolomic responses of plants to different development stages and biotic-abiotic conditions have been investigated in crop species, such as cereals (wheat, barley, rice), tomato and potato, and in some model plants, like the dicot *Arabidopsis thaliana* (Allwood et al., 2006). However, these studies are less developed in *Brachypodium distachyon*, the annual temperate grass selected as model plant for the monocots (Draper et al., 2001, IBI, 2010).

Over the past decade, *Brachypodium distachyon* has emerged as one of the preeminent model plant species, with tremendous genetic, molecular, and genomic resources (IBI, 2010, Mur et al., 2011, Catalán et al., 2014, Gordon et al., 2014). Its flagship plant genome now serves as an anchor for genomic studies across the temperate Pooideae grasses and monocots (Lyons and Scholthof, 2015). Its small genome size, compact genome (e. g. low levels of repetitive DNA), diverse ecological tolerances, ready propagation under controlled growth conditions, and considerable existing molecular and genomic resources make this plant an excellent candidate for addressing fundamental questions in comparative genomics and ecological studies and for its transference to cereal and biofuel crops (Catalán et al., 2014).

The analysis of the intraspecific diversity in *B. distachyon* is under way through the nuclear and organellar resequencing of 54 diverse natural accessions (Gordon et al., 2014; and unpublished data). Phenotypic and metabolomics studies conducted to date in *B. distachyon* have mostly focused on relevant agricultural traits, such as plant height, biomass, flowering time, seed size, seed production and vernalization requirements (Draper et al., 2001, Opanowicz et al., 2008, Filiz et al., 2009, Vogel et al., 2009), and stress-tolerance related metabolites (Allwood et al., 2006, Parker et al., 2008, Parker et al., 2009, Pasquet et al., 2014, Onda et al., 2015, Shi et al., 2015).

Recently, the demonstration that the model plant was not one but three species (Catalán et al., 2012) opened the way to a thoroughly comparative genomic study of this diploid-polyploid complex, which include the model grass plant *B. distachyon* and its close allies *B. stacei* and *B. hybridum*, which show, respectively, 2n=10, 20 and 30 chromosomes (Catalán et al., 2012, 2014). These three cytotypes were previously attributed to different ploidy levels of the same taxon *B. distachyon* s. l. (Robertson, 1981); however, phylogenetic, cytogenetic and phenotypic analyses demonstrated that they should be treated as different species. They consist of two diploids, each with a different chromosome base number [*B. distachyon* (x=5, 2n=10); *B. stacei* (x=10, 2n=20)], and their derived allotetraploid *B. hybridum* (x=5+10, 2n=30). Phylogenetic analyses indicated that the more basally-diverging *B. stacei* and the more recently evolved *B. distachyon* emerged from two independent lineages, confirming their contribution as genome donors of *B. hybridum* (Catalán et al., 2012, 2014).

Regarding their broad phenotypic and ecological features, individuals of *B. distachyon* have overall small stature, require vernalization and are distributed at higher elevations, those of *B. stacei* are morphologically tall, do not require vernalisation and grow mostly in coastlands or at lower altitudes, and those of *B. hybridum* tend to be physically large, generally lack vernalisation requirements and grow in intermediate altitudinal places (Opanowicz et al., 2008, Catalán et al., 2012, López-Alvarez et al., 2015). Statistical analysis of morphometric traits showed that five characters (stomata leaf guard cell length, pollen grain length, upper glume length, lemma length, and awn length) significantly discriminated between the three species when they were grown under controlled greenhouse conditions (12 inbred lines) and showed stability in 24 additional wild populations (Catalán et al., 2012). However, representation of the three circum-Mediterranean species was biased towards the more exhaustively sampled populations of the western Mediterranean region. This was particularly critical for *B. stacei*, a species that was only known from its type locality at the time of its description (Catalán et al., 2012), and for which no other statistically analyzed phenotypic data has been provided to date despite its known distribution in other native circum-Mediterranean localities (López-Alvarez et al., 2012, 2015).

Recently, López-Alvarez *et al*., (2012) provided an alternative and reliable genetic method to differentiate the individuals of the three species using a DNA barcoding system using three loci, the plastid *trn*LF region and the nuclear multicopy ribosomal ITS spacer and the low copy Gigantea (GI) gene, which successfully discriminated between the three species. Interestingly, this study also demonstrated the existence of different bidirectional crosses that likely gave rise to the allotetraploid *B. hybridum*. This was confirmed through the analysis of the maternally inherited plastid haplotypes in this species; the majority of the surveyed *B. hybridum* individuals had inherited a maternal *B. stacei*-like plastome but some of the accessions showed a maternal *B. distachyon*-like plastome (López-Alvarez et al., 2012). The recurrent, polyphyletic and polytopic origin of this allotetraploid species was supported by ITS and GI evolutionary analyses, which revealed distinct relationships of the *B. hybridum* sequences to different parental geographic haplotypic groups, though all the studied hybrids correspond to what is considered to be the same allopolyploid species (López-Alvarez et al., 2012, Catalán et al., 2016b). Nonetheless, the potential phenotypic differences between these two types of reciprocal hybrids have not been investigated to date.

Metabolomics is considered to represent the ultimate level of 'omic' analysis, facilitating the testing of many biological hypotheses based on the statistical support obtained from high-throughput processing of samples (Allwood et al., 2006, Draper et al., 2013), and references therein). Different metabolomics studies have been used to identify different metabolic pathways, wild type and mutant accessions, and sensitive *vs* tolerant lines to biotic and abiotic stresses in plants (Allwood et al., 2006). In *Brachypodium distachyon*, metabolomic analyses have shown to be useful for identifying the main metabolites produced in responses to fungal diseases (Allwood et al., 2006, Pasquet et al., 2014), to temperature-salinity (Onda et al., 2015) and drought (Shi et al., 2015) stresses, and the dynamics of host/pathogen interactions (Parker et al., 2008, 2009).

Non-targeted metabolite fingerprinting is a technique designed to provide a relatively comprehensive view of the metabolome that can be used to test competing hypotheses in organisms (Draper et al., 2013) where prominent changes in the metabolome are revealed without specifically identifying individual metabolites. This method, originally based on Fourier-transform infrared (FT-IR) spectroscopy, was successfully applied to discriminate between control and abiotically stressed lines (Johnson et al., 2003) and responses between tolerant and sensitive lines to fungal attack in plants (Allwood et al., 2006). An additional advantage of metabolite fingerprinting is that the robustness of results can be tested by validation of the analysis using different biological replicates as training and test sets, respectively (Draper et al., 2013). Nonetheless, the combined use of 'first-pass' metabolic fingerprinting and ultra-high accurate mass metabolite profiling, based on direct-injection ESI-MS, which facilitates the identification of particular metabolites, allow for a deeper understanding of the biochemical processes involved in the investigated case studies.

Currently, the increased accuracy of mass spectrometry actually promotes ESI-MS from a merely fingerprinting technique to a metabolite profiling tool, which combined with MS/MS capabilities improves the structural information of the molecules (Draper et al., 2013). A preliminary metabolic fingerprinting analysis conducted in different accessions of diploid *B. distachyon* found different metabolic profiles related to geography (Opanowicz et al., 2008). However, no metabolomic study has been performed to date in *B. stacei* and *B. hybridum*.

The new evolutionary and genomic findings within the *B. distachyon* s. l. complex taxa have set the stage for high definition research of the unusual genomic diversity between and within the species of this complex. The nuclear and organellar genomes of *B. stacei* and *B. hybridum* are being sequenced and will serve, together with *B. distachyon*, as a model system for investigating the origins and consequences of the speciation and polyploidization events (Catalán et al., 2014; and unp. data) that might parallel those of economically important cereals (e. g., wheats; Marcussen et al., 2014). Despite these advances, the phenotypic and metabolomics studies of the three species of the complex are still incomplete or have not been performed yet. Given the importance of these investigations for future GWAS analysis, the objectives of this study are, 1) to analyse the phenotypic variation of a large representation of individuals (and populations) of *B. distachyon*, *B. stacei* and *B. hybridum* collected across their respective native distributions in the circumMediterranean region and in some non-native sites; 2) to test the value of potentially informative morphological traits to discriminate between the three species and within geographic ranges and biological origins (*B. hybridum* only) of each species; 3) to comparatively analyse the metabolite profiles of native accessions of *B. distachyon*, *B. stacei* and *B. hybridum*; 4) to test the value of potentially informative metabolomic traits to discriminate between the three species; 5) to analyse the potential association of phenotypic and metabolomic variation between the three species of the *B. distachyon* s. l. complex.

MATERIALS AND METHODS

Sampling

An enlarged sampling was performed in order to increase the representation of populations and individuals of the three *B. distachyon* s. l. complex species in their respective native circumMediterranean regions and in few non-native areas of *B. hybridum* (Fig. 1, Table S1). The aim was to cover as much intraspecific phenetic and environmental variability as possible, considering that geographic distribution and environmental variability might affect phenetic variability. Infraspecific phenetic diversity for each of the three species under study has been evidenced in previous studies (Vogel et al., 2009, Catalán et al., 2016b). Additionally, an environmental niche model study indicated that *B. distachyon*, *B. stacei* and *B. hybridum* show overlapping but different environmental niches in their native circumMediterranean region where each species presents a different range of variation for different sets of environmental parameters (López-Alvarez et al., 2015). Also, intraspecific environmental variability has been recorded in the three taxa (Manzaneda et al., 2012, Manzaneda et al., 2015, Shiposha et al., 2016). A total of 1050 individuals, of which 870 were newly collected ones, from 174 wild populations of *B. distachyon* (227 individuals, 44 populations), *B. stacei* (146 ind., 30 pop.) and *B. hybridum* (497 ind., 100 pop.), plus the 180 individual samples from the 6 inbred lines of *B. distachyon* [Bd21(type), ABR1]; *B. stacei* [ABR114, type], and *B. hybridum* [ABR113 (type), ABR110, ABR117] employed in the study of Catalan *et al*., (2012), were used in the phenotypic analysis. The new samples were collected in the field or were obtained from herbaria and germplasm banks. Seed from the inbred lines (several generations of selfing) and from new wild germplasm collections (first generation individuals mostly derived from different mother plants) were germinated and grown under standard greenhouse conditions following Catalán *et al*., (2012). All the studied materials were analysed phenotypically when they reached maturity (e. g., flowering and fruiting stages). The geographic origins and nature [wild (W), herbaria (H), seed bank (S) or inbred (I) plants] of all the studied samples are indicated in supplementary Table S1. The taxonomic identity of all the new samples was corroborated through DAPI-staining chromosome counting and/or DNA barcoding methods following the procedures indicated in López-Alvarez *et al.,* (2012). Herbarium vouchers of the newly collected materials have been deposited in the JACA and Unizar (University of Zaragoza) herbaria.

Phenotypic analysis

Phenotypic analysis was performed using the same 15 potentially informative morphoanatomical characters that were employed to separate and to identify the three species of the *B. distachyon* s. l. complex in a previous study (Catalán et al., 2012). Twelve of the characters were quantitative [(Plant) Height (H); Second Leaf Length (SLL); Second Leaf Width (SLW); (Stomata) Leaf Guard Cell Length (LGCL); Inflorescence Length (IL); Spikelet Length (total, without awns; SLa); Spikelet Length (from base to 4^{th} lemma, without awns; SLb); Upper Glume Length (UGL); Lemma Length (LL); Awn Length (AL); Caryopsis Length (CL); Pollen Grain Length (PGL)], and three were discrete characters [Number of Nodes of Tallest Culm (NNTC); Number of Spikelets per Inflorescence (NSI); Number of Flowers per Inflorescence (NFI)] (Tables 1, S2). Macromorphological characters were measured with a hard ruler under a dissecting microscope. Microanatomical characters (LGCL; PGL) were measured under a microscope using an ocular micrometer. For measurements of the stomata leaf guard cell length, abaxial epidermises were peeled off from dried leaves which were pre-treated in a 90% lactic acid solution for 8 hours. Up to ten individuals (specimens) per population were used for assessment of morphological characters. When possible, five measurements were taken for each character in each individual and the corresponding averaged values were used in the analyses. Statistical analyses were performed separately for wild vs inbred + wild individuals (data from inbred individuals was retrieved from Catalán *et al*., (2012). Discriminant analysis was also performed for wild vs inbred + wild individuals (see below).

Simple statistic descriptors of the intra-species and inter-species phenetic diversity (mean, range, standard deviation, box plots of median, range and percentiles) were calculated from the data. The analysis of the inter-species response variables was estimated through one way ANOVA chi-square tests or through nonparametric Kruskal–Wallis tests when the variables complied or not, respectively, with requirements of normality (this was tested through Kolmogorov-Smirnov (K-S) tests; see Table S2). Multiple pairwise comparisons of means were based on Tukey's tests for groups with unequal samples sizes. Inter-species response variables were evaluated through a multicollinearity analysis in order to determine which characters were correlated with each other in the common data set and in each of the species data sets; a matrix of Spearman correlation coefficients was obtained by averaging the values from each individual in each case. Comparative analysis of variables from wild populations *vs* inbred lines was performed using averaged values and through pairwise Mann-Whitney (U) tests. In all cases significant tests were performed for the null hypothesis (H0) of $\mu I=\mu W$, where μI and μW correspond to averaged trait values of inbred lines and wild populations, respectively. All the statistical analyses were conducted with the software SPSS v. 15.

Multivariate analysis of phenotypic traits

Multivariate Principal Component Analysis (PCA) of the 15 variables was performed to examine the structure of the taxa, to assess if the observed groupings were consistent with the taxonomic circumscriptions proposed for the three species of the *Brachypodium distachyon* s. l. complex, and to evaluate the level of covariation in variables. Averaged values of the 15 morphoanatomical characters were estimated for the 174 wild populations and 6 inbred lines of *B. distachyon*, *B. stacei* and *B. hybridum*. The contribution of each character to the coordinate axes that accumulate the highest percentages of variance was calculated by covariance and variance matrices of the samples with respect to the new axes using PAST v. 2.17 (Hammer et al., 2001). Further PCAs were conducted in each of the *B. distachyon*, *B. stacei* and *B. hybridum* subgroup samples following the procedure of the previous search. These independent analyses would allow estimation of the intraspecific substructure of the taxa and calculation of the participation of different morphological characters to the separation of intraspecific groups within each species.

A classification Discriminant Analysis (DA, cross-validation) was conducted with all the variables (15) and samples (174 wild populations and 6 inbred lines) to determine the highest probability membership group of the samples (Legendre and Legendre, 1998). The reference samples for each species's group were the respective type specimens (*B. distachyon*: Bd21; *B. stacei*: ABR114; *B. hybridum*: ABR113). The identification of the more discriminating variables was done by means of Fisher's coefficient (Fisher, 1936, Anderson, 1996) at the significant threshold value of 0.05. The posterior probability of classification of each sample and the Wilks' Lambda value of each discriminant function were calculated. A Wilks' Lambda value closer to zero indicated a better discrimination between the predefined groups. DA was run in SPSS v. 15. Further DAs were also performed following the same procedure indicated above within each of the *B. distachyon*, *B. stacei*, *B. hybridum* groups aiming to classify the samples into intraspecific groups, using as references for each subgroup flag samples from the intraspecific PCA analyses (see Results).

Metabolomic analysis

Sampling for metabolomic analysis was performed in a subset of populations from the three studied species (Table S1). Individuals from 12 populations or inbred lines (5 of *B. distachyon*: 115F, 160F, 162F, 480F, 484F; 3 of *B. stacei*: 114F, 129F, 485F, and 4 of *B. hybridum*: 137F, 176F, 260F, 333F), representing 12 different ecotypes, were grown under standard greenhouse conditions and used in the metabolomic study. A hierarchical metabolomics approach was used to identify and annotate metabolites discriminating the three species. Non-targeted nominal mass metabolite fingerprinting was followed by in depth data mining and ultra-high accurate mass metabolite profiling of explanatory *m/z* bins. Data base searches, MS^n fragmentation analysis and comparison with available standards aided signal annotation at different Metabolomics Standard Initiative (MSI) levels of identification (Sumner et al., 2007).

Metabolite fingerprinting was performed using Flow Infusion Electrospray ionisation Mass Spectrometry (FIE-MS). For this, sample extraction process and mass spectrometric analysis was done following Parker *et al.,* (2009) and Draper *et al.,* (2013). This process involved the use of a single-phase extraction solvent (chloroform: methanol: water, 1: 2.5: 1, v: v: v) optimized for recovery of a wide range of metabolites, offering relatively comprehensive coverage of the metabolome. Nominal mass FIE-MS analysis was performed using a Linear Trap Quadrupole (LTQ) mass analyzer (Finnigan LTQ; Thermo-Finnigan, San Jose, CA), which generated metabolite fingerprints in both positive and negative ionisation mode. Ion intensities were detected in the scan range between *m/z* 50 and 1150 that was sub-divided in four small mass ranges for better signal acquisition (low range, *m/z* 15-200; high1 range, *m/z* 180-620; high2 range, *m/z* 600-880, and high3 range, *m/z* 860-1150), and raw data dimensionality was reduced by electronically extracting signals with ± 0.1 Da mass accuracy. Mass spectra were combined in a single intensity matrix (runs x *m/z* ratios) for each ion mode. Data from intensity matrix was log-transformed and normalized to the total ion count (TIC) before further statistical analysis. Initially, data mining and feature selection was performed using Random Forest in R package *FIEms-pro* as reported previously (Team, 2010, Enot et al., 2008).

Ionization products (*m/z*) identified after data mining were annotated by searching accurate *m/z* through the MZedDB database (Aberystwyth University) (http://maltese.dbs.aber.ac.uk:8888/hrmet/index.html) at < 5 ppm mass accuracy. Accurate masses from species representative extracted samples were acquired using Exactive LC-MS system (Thermo-Scientific) operating in flow-infusion mode. As several overlapping solutions predicting the presence of different metabolites were often possible, the most likely combination of ions putatively identifying a specific metabolite were confirmed by comparing their MS^n fragmentation patterns with available standards. MS^n fragmentation was carried out on Finnigan LTQ (Thermo-Finnigan, San Jose, CA) using ion trap, full MS mode by using a normalized collision energy of 30.0 V. Samples were injected at a flow rate of 3.0 µL / min with activation (Q) of 0.250 and activation time of 30.0 ms. 30 scans were used to acquire fragmentation data with an isolation width of 1.0 *m/z*.

Statistical and multivariate analysis of metabolomic traits

Metabolomic data were subjected to simple statistical analysis of the inter-specific diversity (mean, range, standard deviation, box plots of median, range, intervals) and the response variables were estimated through one-way ANOVA chi-square tests and through nonparametric Kruskal-Wallis for parametric and non-parametric variables, respectively, to determine which metabolites were significantly different between the *B. distachyon*, *B. stacei* and *B. hybridum* ecotypes. Only metabolites that were annotated at different MSI levels of identification (see Supplementary data) were used in the multivariate analysis. DA was conducted with the metabolomic data; this consisted of a supervised projection method where discrimination between groups was based on the spatial classification of ecotypic samples in

2D projections using a priori knowledge of species projections. The Fisher's coefficient (p = 0.05) was used to identify the more discriminating variables, and the posterior probability of classification of each sample and the Wilks' Lambda value of each discriminant function were also calculated. All statistical analyses were conducted in SPSS v. 15.

Associated phenotypic and metabolomic variation

The potential association of phenotypic and metabolic variation between the three species of the *B. distachyon* s. l. complex was estimated through correlation analysis using Pearson coefficients. Class means (at ecotype level) of both the 15 phenotypic measurements and the 434 metabolic variables (*m/z* intensity values) were used for correlation analysis as individual phenotypic measurements could not be attributed to the metabolomic data. Correlation analysis was performed using *rcorr* in R package *Hmisc* and resulting p-values were corrected by Bonferroni method.

RESULTS

Interspecific phenotypic variation

Statistical descriptors and box and whisker plots (Table 1, Fig. 2) summarized the inter and intraspecific phenotypic diversity detected by the 15 analysed morphological characters across the studied wild populations of the three species. Significant differences ($P<0.001$) were found in 13 variables for different combinations of species (Table 1): eight characters discriminate all three species from each other (LGCL, PGL, H, SLW, IL, NSI, LL, AL) (Fig 2a), four characters discriminate between *B. distachyon* vs. *B. stacei* and *B. hybridum* (SLL, SLa, SLb, CL) (Fig. 2b), and one character discriminate *B. hybridum* from the diploid species (NNTC) (Fig. 2c). Only two characters did not significantly discriminate the species (NFI, UGL) (Table 1; Fig. 2d). The individuals of *B. hybridum* showed mean values significantly higher for three characters, stomata guard cell length (LGCL; $\bar{x}$ =29.3 ± 3.3μm), pollen grain length (PGL; $\bar{x}$ =38.7 ± 0.121μm) and number of nodes of tallest culm (NNTC; $\bar{x}$ =5.7±2.4), than individuals from the diploid species (*B. distachyon*, $\bar{x}$ =22.5; $\bar{x}$ =30.4; $\bar{x}$ =4.0; *B. stacei*, $\bar{x}$ =25.2, $\bar{x}$ =33.9, $\bar{x}$ =4.4), while individuals of *B. stacei* showed mean values significantly higher for six characters, plant height (H; $\bar{x}$ =43.6 ± 17.4), second leaf width (SLW; $\bar{x}$ =2.7±0.9), inflorescence length (IL; $\bar{x}$ =5.3±1.5), lemma length (LL; $\bar{x}$ =9.4±1.3), awn length (AL; $\bar{x}$ =12.4±2.7), and number of spikelets per inflorescence (NSI; $\bar{x}$ =3.3±0.8) than individuals of *B. hybridum* and *B. distachyon* (Table 1; Fig. 2a-c). Individuals of *B. distachyon* were characterized by smaller and shorter leaf, inflorescence, spikelet, lemma, awn and caryopsis than those of the other species; they also showed few nodes in the stem and less spikelets and flowers per inflorescence (Table 1; Fig 2). Individuals of *B. hybridum* showed intermediate dimensions between those of individuals of its parental species in seven characters (H, SLW, IL; NSI, LL, AL, CL) (Table 1; Fig. 2).

When mean value data obtained from the analysis of wild individuals (W; wild *vs* wild) were compared with those obtained from inbred individuals (I; inbred *vs* inbred) (Table 2; W-I Mann-Whitney test: wild *vs* inbred) three characters (PGL, SLA, NFI) did not show significant differences between the two groups in the three species, two (H, NSI) in *B. stacei* and *B. hybridum*, and two (LGCL, AL), four (IL, SLB, UGL, LL) and one (SLE) in *B. distachyon*, *B. stacei* and *B. hybridum*, respectively. From the three common stable traits in both data sets, PGL discriminated between all three species and SLA between *B. distachyon* and *B. stacei* or *B. hybridum*; NFI did not discriminate between species (Table 2). LGCL, LL and AL also discriminated between all three species, and SLL and SLB between *B. distachyon* and *B. stacei* or *B. hybridum* in both data sets but with different means in W and I for some species, SLW between the three species in W (but only between *B. distachyon* and *B. stacei* or *B. hybridum* in I), and CL between *B. distachyon* and *B. stacei* or *B. hybridum* in

W (and between *B. stacei* and *B. distachyon* or *B. hybridum* in I) (Table 2). Two traits that significantly discriminated between the three species within the inbred lines (I), discriminated only between *B. hybridum* and *B. distachyon* or *B. stacei* (NNTC), or did not discriminate between them (UGL) in the larger data set of wild individuals (W) (Table 2). The Spearman correlation analysis conducted with the phenotypic traits studied in the wild individuals of *B. distachyon*, *B. stacei* and *B. hybridum* revealed significant correlations ($p<0.001$) between several characters [SLA/SLB (0.89), IL/NSI (0.75), H/IL (0.70), SLW-SLL (0.69), H/SLL (0.66), H/NSI (0.65), IL/SLA (0.65), NFI/SLA (0.62), LL/SLA (0.59), NFI/SLB (0.59), LL/SLB (0.56), NNTC/SLL (0.56), LGCL/PGL (0.54), H/SLW (0.53) and H/NNTC (0.52)] (Table S3).

The PCA revealed that 93.3% of total variation of the 15 analysed characters could be explained by the first three principal components which accumulated 79.2%, 10.4% and 3.6% of the variance, respectively (Table S4, Fig. 3). Three characters were identified as the most important contributors to the positive and negative extremes of the first components of the PCA. Plant height (0.98), pollen grain length (0.88) and stomata leaf guard cell length (-0.61) showed the highest contributions to the first, second and third components, respectively (Table S3). The impact of these components on the hierarchical structure of the three species was visualized in a 2D PCA plot (Fig. 3). Population samples of the three species overlapped in the two-dimensional space created by the first two components. The highest overlap was observed between the minimum convex polygons of *B. stacei* and *B. hybridum* (Fig. 3).

The DA conducted over all 174 wild populations of *B. distachyon*, *B. stacei* and *B. hybridum* using the data from the 15 analysed phenotypic traits separated the three species in the two-dimensional plot constructed with the two functions (Fig. 4a). *B. distachyon* clustered separately from *B. stacei* and *B. hybridum* along the first axis of the plot, which explained 68.2% of the total variance, whereas the last two species separated along the second axis, which explained 31.8% of the variance. Catalán *et al.* (2012) also found similar discrimination among the three species when the DA was performed only with individuals from the 6 inbred lines, though sampling of *B. stacei* was reduced to the type specimen (ABR114). Equivalent results were obtained when DA was performed with the 6 inbred lines added to the 174 wild populations (Fig. 4b); the three species showed similar clustering patterns in the 2D plot which had functions 1 and 2 explaining 66.8 and 33.2% of the total variance, respectively. All *B. distachyon* populations were correctly classified (100%) both including (46 samples) and excluding (44) the inbred lines (Table 3). However, only 25 (83%) of 30 wild populations of *B. stacei* were correctly classified (with the 5 remaining samples B891, B921, B621, Bra286 and B100-H141 classified as *B. hybridum* (17%)), and only 25 (81%) of 31 wild + inbred samples were correctly assigned (with 6 remaining samples classified either as *B. hybridum* (5, 17%) or *B. distachyon* (BGE044241, 3%)). Most samples of *B. hybridum* were correctly classified in both analysis (92%); 92 out of 100 wild populations, and 95 out of 103 wild + inbred samples, were correctly assigned, with the 8 remaining samples classified either as *B. stacei* (5: B124, 333F, BGE044239, BGE044247, Mog; 5%) or *B. distachyon* (3: BGE044243, B741, Bra299; 3%) in both cases (Table 3). Up to ten and five phenotypic characters showed strong correlations to the first and second canonical discriminant functions, respectively (Table S5), with Wilk´s Lambda values of 0.12 and 0.44 ($p<0.001$), respectively. Of those, three (LGCL, CL and PGL) showed the highest contributions to function 1 and one (IL) to function 2 in the wild populations and the combined inbred lines and wild populations data sets [LGCL (0.54, 0.56), CL (0.47, 0.46) and PGL (0.42, 0.44); IL (0.52, 0.53)] (Table S5).

Intraspecific phenotypic variation

The DAs conducted at the intraspecific level in *B. distachyon*, *B. stacei* and *B.*

hybridum using the 15 phenotypic traits showed significant differences for some traits and different geographical groupings of populations in one and another studied species. In *B. distachyon*, the two-dimensional plot constructed with the first two discriminant functions that explained 79.7% and 10.8% of the total variance indicated the separation of four groups of Iberian populations (Fig 5a). Northeastern Iberian populations (Aragón, Navarra, Lleida) clustered in the upper left area of the plot, Northwestern Iberian populations (Valladolid, Palencia) and southern Iberian populations (Andalucía) plus one additional population from southern Spain (Cadiz) in the lower left and middle areas, and central Iberian populations (Albacete, Cuenca, Madrid, Rioja) in the upper right area. The characters that showed higher correlations to functions 1 and 2 were H (0.56) and UGL (0.66), AL (0.46) and NNTC (0.46) ($p<0.001$), respectively, with Wilk´s Lambda values of 0.012 ($p<0.001$) and 0.15 ($p=0.058$) (Table S6), respectively. The height of the plant (H) was significantly different between the central ($\bar{x}=42.2^{a}$) and the northwestern ($\bar{x}=32.2^{b}$) groups, which in turn showed taller individuals than those of the northeastern ($\bar{x}=18.6^{c}$), and southern ($\bar{x}=13.8^{c}$) Iberian groups (Table 4). The length of the upper glume (UGL) significantly separated the southern ($\bar{x}=4.3^{b}$) populations from the others ($\bar{x}=6.4^{a}$), the number of nodes in the tallest culm (NNTC) the northeastern populations ($\bar{x}=2.7^{b}$) from the rest ($\bar{x}=6.4^{a}$), the length of the awn (AL) the northeastern ($\bar{x}=11.2^{a}$) from the southern ($\bar{x}=9.5^{b}$) populations, and the number of spikelets per inflorescence (NSI) the central ($\bar{x}=3.0^{a}$) from the northeastern and southern ($\bar{x}=1.8^{b}$) populations (Table 4).

In *B. stacei* the 2D plot constructed with the first two discriminant functions that accumulated 79.4% and 11.4% of the total variance classified three groups of circumMediterranean populations (Fig 5b). The Iranian populations clustered at the upper right area of the plot, and the Balearic populations at the lower right area; they were clearly separated from the other populations along function 1. Populations from Israel clustered close to populations from Almeria (S Spain) in the upper middle area of the plot, those from the Canary Islands in the middle central area, those from southern Spain and Mahgreb (Tunisia) in the leftmost central area, and one population from Greece in the lowest left area (Fig. 5b). The phenotypic traits that showed higher correlations to functions 1 and 2 were IL (-0.11) and SLB (0.18) and SLA (0.17) ($p<0.001$) (Table S7), respectively, with Wilk´s Lambda values of 0 ($p<0.001$) in both cases. The pollen grain length (PGL) significantly discriminated the Iranian populations, which showed longer pollen grains ($\bar{x}$=47.2^{a}) than the rest ($\bar{x}$=32.3^{b}) (Table 4). IL, NNTC and SLL traits separated southern Spain ($\bar{x}$=3.7^{b}; $\bar{x}$=2.8^{b}; $\bar{x}$=9.2) from Balearic Island ($\bar{x}$=6.1^{a}; $\bar{x}$=6.2^{a}; $\bar{x}$=4.3) populations, NNTC and SLL southern Spain from the Israel ($\bar{x}$=5.8^{a}; $\bar{x}$=5) populations, and SLL southern Spain from Iran ($\bar{x}$=4.5) populations; the remaining populations showed intermediate measurements for those traits ($\bar{x}$=5.2^{ab}; $\bar{x}$=4.6^{ab}; $\bar{x}$=6.9) (Table 4).

In *B. hybridum* the first two discriminant functions of the two-dimensional DA plot that explained 42.7% and 31.4% of the total variance did not show a clear-cut geographical clustering of circumMediterranean populations though they separated two main groups along the first axis (Fig 5c). Populations from northeastern Spain and the Balearic islands clustered in the left area of the plot whereas those from the Middle-East, the Mediterranean basin, southern Spain and the Canary Islands clustered predominantly on the right area. The most influential characters were H (0.51), SLW (0.44) and CL (0.40), and NNTC (0.57), UGL (0.48), and NFI (0.42), which were highly correlated to the first and second functions ($p<0.001$), respectively (Table S8), with Wilk´s lambda values of 0.02 and 0.08 ($p<0.001$), respectively. The height of the plant separated the taller Mediterranean and Canary Islands individuals ($\bar{x}$=47^{a}; $\bar{x}$=45.8^{a}) from the shorter Balearic Islands and northern Spain individuals ($\bar{x}$=18.1^{c}; $\bar{x}$=21.5^{c}), whereas individuals from other regions (southern Spain $\bar{x}$=36.7^{b}; Middle East $\bar{x}$=35.3^{b}) showed intermediate statures (Table 4). Caryopsis length (CL) and width of the second leaf (SLW) differentiated the individuals from Middle East and Canary Islands ($\bar{x}$=7.4^{a}; $\bar{x}$=2.7^{a}) from those of northern Spain and Balearic Islands ($\bar{x}$=6.2^{c}; $\bar{x}$=1.7^{c}), whereas the Mediterranean and southern Spain individuals showed intermediate values ($\bar{x}$=6.6^{b}; 2.4$^{ab;b}$) (Table 4). The number of nodes in the tallest culm was higher in Mediterranean and southern Spain individuals ($\bar{x}$=6.8^{a}; $\bar{x}$=6.2^{a} respectively; Table 4) with respect to those of Middle East ($\bar{x}$=5.2^{b}) and Balearic Island, Canary Islands and northern Spain ($\bar{x}$=3.8^{c}; $\bar{x}$=3.3^{c}; $\bar{x}$=2.8^{c}) individuals.

Interspecific metabolomic variation

Metabolite fingerprinting analysis resulted in a total of 2219 nominal *m/z* in combined positive and negative ionisation datasets in the 12 studied ecotypes of *B. distachyon*, *B. stacei* and *B. hybridum*. However, only 693 metabolite signals showed significant differences between species based on Random Forest feature selection, and of these only 434 nominal *m/z* signals could be further annotated using targeted accurate mass *m/z* search through MZedDB database (Table S9). Where more than one *m/z* signals resulted in the annotation of same metabolite e.g. due to various adducts formation, the most likely adduct was selected based on either, the most abundant adduct or by giving preference for $[M+H]^{1+}$ and $[M+K]^{1+}$ adduct in positive ion mode and $[M-H]^{1-}$ adduct in negative ion mode over the other adducts. The other duplicate adducts were however kept in the annotation list of 434 *m/z* signals (in plain text rather than bold) (Table S9) as they give aided confidence in the annotation of *m/z* signals. These *m/z* signals with duplicate annotations were however later removed from the DA, details of which are provided below. Some of the annotation results were confirmed by comparing MS^{n} fragmentation patterns of *m/z* signals with that of available standard's (see Table S10 for the list of annotated *m/z* signals).

Statistical descriptors and box and whisker plots indicated that 434 fingerprint *m/z* signals were able to significantly discriminate between the three species (Tables S11, S12; Fig. 6). Of these, several positive (e. g., p214.09, p147.09, p182, p296.18, p139.9, p816.54, p235.09, p381.18) (Fig. 6a) and negative (e. g., n281.18, n385.18, n346.09, n315.18, n163, n203.09, n135, n179.09) (Fig. 6b) *m/z* discriminated the ecotypes of *B. distachyon*, *B. stacei* and *B. hybridum* between each other (Table S12).

The DAs conducted over the 12 ecotypes of *B. distachyon*, *B. stacei* and *B. hybridum* using the data from the 434 (positive 217, and negative 217) metabolomic traits discriminate the three species in the two-dimensional plots formed by the two functions (Table S11; Fig. 7). Removing *m/z* signals of same annotations showing different adducts does not alter DA classification results (Tables S9, S11; Fig. S1). The five ecotypes of *B. distachyon* clustered separately from those of *B. stacei* and *B. hybridum* along the first axis of the plot, which explained 84.7% (positive data set) or 80% (negative data set) of the total variance, whereas the ecotypes of the last two species separated respectively along the opposite extremes of the second axis, which explained 20% (positive data set) or 15.3% (negative data set) of the variance. Both positive and negative metabolites were significantly correlated with the first (Wilk´s Lambda = 0; $p<0.001$) and second (Wilk´s Lambda = 0.01 (positive data set), 0.02 (negative data set); $p<0.001$) functions of their respective analysis though their correlation values were usually low (Table S11). The ecotypes of each species were correctly classified to their respective groups in all cases (100%).

Association of phenotypic traits and metabolites

The Pearson correlation analysis between phenotypic traits and 434 fingerprint *m/z* signals indicated that the highest significant Bonferroni corrected p-values < 0.05 correlations were for pollen grain length (PGL) and lemma length (LL) (Table 5) to discriminate the three species. PGL showed significant correlations with 10 metabolite signals (hydroxybutyrate, threonate, shikimate, ^{13}C isotope of shikimate, quinate, ^{13}C isotope of quinate, sinapate, sedoheptulose 7-phosphate, ADP-glucose, PG(18:1(11Z)/22:6 (4Z,7Z,10Z,13Z,16Z,19Z)), and LL showed significant correlations with six metabolites (*O*-Phosphohomoserine and lipids tentatively assigned as PC(16:0/18:2(2Z,4Z)), SQDG(16:0/16:1(11Z)), PC(18:3(8E,10E,12E)/18:3(8E,10E,12E)) (PC(36:6)), PC(18:0/18:3(9Z,12Z,15Z)/0:0), PG(18:0/20:3(5Z,8Z,11Z))) (Table 5 and Fig. S2).

DISCUSSION

Phenotypic differentiation is shaped both taxonomically and geographically within the B. distachyon s. l. complex species

The large phenotypic analysis conducted on 1050 individuals from 174 wild populations and 6 inbred lines of *B. distachyon*, *B. stacei* and *B. hybridum* has provided a wealth of data and strong statistical evidence for disentangling the intraspecific phenotypic plasticity and the interspecific differentiation of the three species, once considered cryptic taxa (Garvin et al., 2008, Catalán et al., 2012, López-Alvarez et al., 2012). The considerably increased sampling size of this study with respect to the pioneer work of Catalán *et al.,* (2012) has allowed to also increase the number of significantly discriminating traits between the species from five to eight (Table 1, Fig. 2). To the five characters (stomata leaf guard cell length, pollen grain length, upper glume length, lemma length, awn length) found previously Catalán *et al.,* (2012) to significantly discriminate between the three taxa when inbred lines were grown under controlled greenhouse conditions, the present study adds four more characters (plant height, second leaf width, inflorescence length, number of spikelets per inflorescence) and discards one (upper glume length) for discriminating between wild individuals of the three species. Exhaustive analysis shows that despite an increase of intraspecific phenotypic variability within each species (Tables 1, 2; Fig. 2) when compared to Catalán *et al.,* (2012), the number of discriminant taxonomic traits also raises (from the same 15 original characters) as a consequence of the more robust statistical inference and the underlying evolutionary phenotypic differentiation of the three members of the complex (Catalán et al., 2012, 2014).

This study has also shown geographically-diverse phenotypic data for the poorly known species *B. stacei* (Tables 1, 2, S1; Fig. 2). This taxon emerges as the tallest plant and with some of the largest features (inflorescence, no. spikelets/inflorescence, lemma and awn) of the three species of the complex, oversizing the measurements of the allotetraploid *B. hybridum* for those traits (Table 1, Fig. 1). Additionally, this study confirms previous findings of Catalán *et al.,* (2012) like smaller stature and shorter features (12 out of the 15 studied traits) of *B. distachyon* with respect to its two congeners. The considerable phenotypic gap observed between the two diploid species *B. stacei* and *B. distachyon* (Table 1; Fig. 2) could be a consequence of their distinct evolutionary origins, large divergence and genomic expressions (Catalán et al., 2012, 2014). The allotetraploid *B. hybridum* shows significantly larger measurements for two non-endoreduplicating plant cell types, stomata guard cell length and pollen grain length, than its two diploid progenitors (Table 1). Correlation between increasing ploidy level and larger pollen grain and stomata guard cell sizes have been reported in other pooids, like *Lolium* (Speckmann et al., 1965), *Bromus* (Tan and Dunn, 1973), and *Dactylis* (Bretagnolle and Lumaret, 1995). These traits could be also used as proxies to differentiate *B. hybridum* from its parents.

The use of morphological traits is considered to be limited, because most of the traits are multigenic, quantitative characters that could be influenced by environmental conditions, plant age, phenological stage or cultivation conditions (Smykal et al., 2008). However, presented data support the stability of the phenotypic characters in natural populations when compared to the propagated inbred lines (Table 3). Most of the studied characters show the same discriminant value to separate between wild, cultivated, or wild and cultivated individuals of *B. distachyon*, *B. stacei* and *B. hybridum* (Tables 3, S5). Furthermore, three of the traits (pollen grain length, spikelet length, number of flowers per inflorescence) have shown to be similarly discriminant among the three species, both in wild and inbred plants. Results of this study suggest that these traits could be genetically fixed and might constitute a valuable tool to separate and identify individuals of the *B. distachyon*, *B. stacei* and *B. hybridum*. However, the precise phenotypic characterization and identification of all individuals is not always possible, as demonstrated by the failure to correctly classify a few individuals of *B. stacei* and *B. hybridum*, erroneously assigned to other species (Table 3, Figs. 4a,b). Because the taxonomic identity of those individuals was confirmed by chromosome counting and/or DNA barcoding, their diverging phenetic features could have resulted from extreme plasticity or a consequence of the restricted number of phenotypic traits used in the study. By contrast, the low percentages of failures detected (up to 20% in *B. stacei*, 8% in *B. hybridum*, and 0% in *B. distachyon*) suggest that the employed morphological traits are good diagnostic features to differentiate these taxa. In a recent updated taxonomic description of these species, five additional qualitative phenotypic traits have been found useful discriminators: leaf blade color to separate all three species, occasional production of short rhizomes to discriminate *B. stacei* and *B. hybridum*, and leaf blade shape, softness and hairiness to separate *B. stacei* from the other two species (Catalán et al., 2016a).

The analysis of the phenotypic variation within each of the three species of the *B. distachyon* complex has also untapped the organization of their intraspecific diversity (Fig. 5). The geographic phenotypic structure observed between the northern, central and southern Iberian populations of *B. distachyon* (Fig. 5a) might reflect different adaptations to environmental conditions (Manzaneda et al., 2015) and could be also indicative of genotypic differences (López-Álvarez & Catalán, unp. data). Also, the observed differences in plant height (H), with central and northern Spanish individuals being significantly taller than southern Spanish individuals (Table 4), has been corroborated in independent phenomic studies of Iberian *B. distachyon* inbred lines (E. Pérez-Collazos & J. Finch, pers. comm.). The broader but less congruent geographic structure of *B. stacei* phenotypes (Fig. 5b) suggests the isolation of circumMediterranean-edge Iranian and continental-island Balearic populations *versus* the proximity of largely disjunct Israel-southern Spain (Almeria) and southern Spanish-Canary Islands populations. Long distance dispersals of seeds have been proposed for *B. distachyon* and *B. hybridum* (Vogel et al., 2009) and could also operate in *B. stacei*. The low geographically structured variation within *B. hybridum* detects however a slight differentiation of the Balearic and northern Spanish populations from the rest (Fig. 5c). It is important to stress, however, that the southern Spanish allotetraploid individuals derived from the unusual cross of maternal *B. distachyon* parent and paternal *B. stacei* parent (cf. López-Alvarez et al., 2012) are morphologically close to other Mediterranean individuals derived from the common cross of maternal *B. stacei* and paternal *B. distachyon* (Fig. 5c). In allopolyploid grasses different bidirectional crosses of parental species might originate the same or different hybrid allopolyploid species (e. g., *Aegylops*; Meimberg et al., 2009). However, our data corroborate the idea of a unique speciation event in the origin of *B. hybridum*, even if its individuals could have originated from alternative bidirectional crosses between different ancestral diploid progenitors (Catalán et al., 2016b).

Metabolomic characterization of B. distachyon, B. stacei and B. hybridum and association of phenotypic-metabolite traits

FIE-MS fingerprinting has provided a preliminary metabolite profile for the three species of the *B. distachyon* complex. The study shows that a large number of metabolites (434) could be used to discriminate between *B. distachyon*, *B. stacei* and *B. hybridum* (Tables

S9-S12; Fig. 6). For example, citrulline content is significantly larger in *B. hybridum* than in its parental species, of which *B. distachyon* shows the lowest concentration (Fig. 6A). Citrulline has been shown to play an important role in transporting and storing nitrogen, and is reported as an important biochemical indicator of plant tolerance to saline and drought stresses (Kawasaki et al., 2000, Kusvuran et al., 2013). In this study, citrulline levels reflect a climatic variation from warmer and more aridic Iberian places (*B. hybridum* ecotypes), through warm but shady places (*B. stacei* ecotypes), to more mesic places (*B. distachyon* ecotypes) (Fig. 1; Catalán et al., 2016a), supporting the different ecological adaptations of the three species' ecotypes to their respective environments. Another example is a phospholipid assigned as phosphatidylcholine(36:6) (PC(36:6)) whose levels were significantly larger in *B. hybridum* than in its parental species (Fig. 6A). Drought stress has been shown to induce changes in the leaf lipid composition by increasing the levels of phosphatidylcholine suggesting specific adaptive alterations in the membrane composition to compromise drought stress tolerance (Vigh et al., 1986, Toumi et al., 2008).

DA analysis indicates not only that each species could be significantly separated from each other (Figs. 7; S1) but that *B. distachyon* falls clearly apart from *B. stacei* and *B. hybridum*, followed by metabolomic differentiation of the later. This pattern parallels what has been observed in the phenotypic analysis (Fig. 4) and in molecular relationships between the species, especially in the plastid genome-based reconstructions (López-Alvarez et al., 2012). Thus, metabolite fingerprinting is concordant with phenotypic analysis within the species *B. distachyon* complex. The Pearson correlation analysis between phenotypic and metabolomics traits indicated a significant association for pollen grain length (PGL) and lemma length (LL) with respectively two distinct groups of metabolites, members of the phenolics biosynthesis and lipids. PGL showed significant correlations with metabolite signals for Shikimate, ^{13}C Isotope of Shikimate, Sinapate, Quinate, ^{13}C Isotope of Quinate as well as Sedoheptulose-7-phosphate, ADP-Glucose, and a PG(40:7). LL correlated mainly with lipids, including phosphatidylcholines (PCs) (Table 5). Since the correlation analysis applied here is only preliminary and these phenotypic traits are among the best markers to discriminate the three species, especially PLG is likely genetically fixed (Tables 2, S3), one has to consider chance: high significant correlations found between metabolites and phenotypic traits might reflect their statistical value to separate the three species, rather than a direct association with the sizes of the pollen grain and lemma length. However, there is evidence that these results indicated a potentially strong link between PGL and lignin / phenolics biosynthesis, and LL and lipid metabolism. PGL can be associated with phenolics composition as it provides structural support to pollen grain, because mature angiosperm pollen grains are covered by three distinct layers of cell walls: (1) an outer exine coating, composed of a tough, chemically resistant biopolymer sporopollenin, which is interrupted by openings called apertures; (2) an inner intine coating, made primarily of cellulose, and (3) a pollen coat, composed of lipids, proteins, pigments, and aromatic compounds that fills the sculptured cavities of the pollen exine wall (Edlund et al., 2004). The sporopollenin is present in the spore / pollen walls of all land plants, comprising both aliphatic (unsaturated lipids), and aromatic (phenolics) components, and is regarded as one of the most recalcitrant biomacromolecules, providing protection against the harsh terrestrial environments including a range of abiotic stresses (de Leeuw et al., 2006, Fraser et al., 2012). Results therefore show that phenolics biosynthesis may be crucial for pollen grain development as they provide structural components to both sporopollenin and pollen coat formation. An alternative explanation is that the levels of accumulation of those metabolites in the different species indicate that some biochemical pathways have or have not been switched on yet. A genome-wide SNP scan study to identify trait-regulatory genomic loci in chickpeas showed the up-regulation of a superior gene haplotype correlated with increased transcript expression of

Ca_Kabuli_CesA3 gene in the pollen and pod of high pod/seed number accession, resulting in higher cellulose accumulation for normal pollen and pollen tube growth (Kujur et al., 2015). Environmental triggers like temperature or drought might also influence availability of metabolites for enzymatic systems regulating pollen grain and lemma length, but gaps in our knowledge of how constrains affect plant survival and seed production are being filled only slowly (Ejsmond et al., 2011).

A number of studies have corroborated the differentiation of the three species of the *B. distachyon* complex, like those based on seed protein data (Hammami et al., 2011), phenotypic and cytogenetic traits and nuclear and plastid phylogenetic markers (Catalán et al., 2012), nuclear SSRs (Giraldo et al., 2012), DNA barcoding (López-Alvarez et al., 2012), isozymes (Jaaska, 2014), and Comparative Chromosomes Painting (CCP; Idziak et al., 2011, Betekhtin et al., 2014). This study shows that metabolomics can discriminate the three species. Furthermore, preliminary metabolite discriminant analysis suggests a closer metabolomic affinity of *B. hybridum* to its maternal *B. stacei* parent than to its paternal *B. distachyon* parent for the studied ecotypes (Fig. 7). The closeness of the allotetraploid hybrid to its *B. stacei* parent, supported by both phenotypic and metabolomic data (Figs. 4, 7) is also in agreement with whole genome sequence (Vogel, com. per.) and environmental data; environmental niche model analyses demonstrated a larger niche overlap and niche affinity of the *B. hybridum* niche to that of *B. stacei* than to the *B. distachyon* niche (López-Alvarez et al., 2015). Because phenotypic and metabolomic data reflect the summed effects of genotypic composition and environmentally-mediated gene expression, larger genomic, phenomic and metabolomic analyses should be conducted on higher numbers of replicates and different ecotypes of the three species to identify the allelic variants and regulatory elements responsible for the observed phenotypic and metabolomics profiles at both, species and ecotype levels. The preliminary phenotypic and metabolomic analyses applied in this study have set the way for future, more exhaustive, GWAS studies.

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SUPPLEMENTARY INFORMATION

A detailed description of phenotypic and metabolomics variables analyzed in inter and intraspecific statistical studies of *Brachypodium distachyon*, *B. stacei* and *B. hybridum* populations is included as Tables S1 to S12 and Figures S1 and S2 in the supplementary information.

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Table 1. Statistics of 15 phenotypic traits and significance tests of their mean values analyzed in individuals from 174 wild populations of *Brachypodium distachyon*, *B. stacei* and *B. hybridum*. Underlined variables are those that significantly discriminate between the three species. N, number of wild individuals analysed. ANOVA (F; d.f. 2) or Kruskal-Wallis (X^2; d.f. 2) tests of variables used for comparisons between species. Superscripts denote Tukey pairwise comparisons between species; means with the same letter do not differ significantly ($p<0.05$). See text and Table S2 for abbreviations of variables.

Species	**LGCL** (µm)	**PGL** (µm)	**H** (cm)	**NNTC**	**SLL** (cm)	**SLW** (mm)	**IL** (cm)	**NSI**	**SLA** (cm)	**SLB** (cm)	**NFI**	**UGL** (mm)	**LL** (mm)	**AL** (mm)	**CL** (mm)
B. distachyon															
N	227	211	191	190	171	174	184	184	187	183	188	191	188	190	184
Minimum	17	21	5,5	1	1,1	0,5	0,92	1	0,92	0,5	4	2,2	5,2	6,3	3,8
Maximum	28	42	56	12	8,2	3,5	5	4	2,4	1,82	13	9,1	11	15,2	7,2
Mean	**22,5**^{a}	**30,4**^{a}	**19,8**^{a}	**4,0**^{a}	**3,0**^{a}	**1,7**^{a}	**2,3**^{a}	**2,1**^{a}	**1,6**^{a}	**1,1**^{a}	**7,9**^{a}	**6,0**^{a}	**7,2**^{a}	**10,7**^{a}	**5,5**^{a}
Std. Deviation	2,2	3,8	11,9	2,4	1,5	0,5	0,8	0,8	0,3	0,2	2,1	1,5	0,9	1,9	0,7
Variance	5,0	14,4	141,8	5,9	2,2	0,3	0,6	0,7	0,1	0,1	4,4	2,3	0,8	3,7	0,4
B. stacei															
N	146	154	86	90	75	82	88	91	90	91	88	90	91	88	123
Minimum	16	22	6,1	1	1,6	1,1	2,3	2	1,3	0,61	4	2,9	6,1	7,5	5,4
Maximum	36	52	76	9	15,1	5	10	5	3,3	2,82	14	8,63	12,6	18,2	8,4
Mean	**25,2**^{b}	**33,9**^{b}	**43,6**^{c}	**4,4**^{a}	**7,4**^{b}	**2,7**^{c}	**5,3**^{c}	**3,3**^{c}	**2,2**^{b}	**1,6**^{b}	**8,5**^{a}	**5,8**^{a}	**9,4**^{c}	**12,4**^{c}	**6,9**^{b}
Std. Deviation	4,4	5,9	17,4	1,7	3,3	0,9	1,5	0,8	0,4	0,4	2,3	1,2	1,3	2,7	0,7
Variance	19,5	35,2	301,7	3,0	11,0	0,7	2,2	0,6	0,1	0,2	5,5	1,4	1,7	7,5	0,5
B. hybridum															
N	497	518	330	340	320	327	347	350	343	340	343	352	349	349	413
Minimum	20	25	3,5	1	1	0,7	1,2	1	1	0,5	2,33	2,3	3	6	5
Maximum	37	57	78	11	15,2	4,3	8	6	4,1	2,96	16	9,8	12,9	18,9	8,9
Mean	**29,3**^{c}	**38,7**^{c}	**35,9**^{b}	**5,7**^{b}	**7,5**^{b}	**2,4**^{b}	**3,5**^{b}	**2,7**^{b}	**2,1**^{b}	**1,5**^{b}	**8,1**^{a}	**5,9**^{a}	**8,9**^{b}	**11,6**^{b}	**6,7**^{b}
Std. Deviation	3,3	5,6	15,3	2,4	3,3	0,7	1,2	1,1	0,5	0,4	2,8	1,5	1,8	2,7	0,8
Variance	10,8	31,2	235,3	5,5	11,0	0,5	1,4	1,2	0,2	0,2	7,7	2,2	3,3	7,4	0,6
X^2	411,6	322,1	164,5	82,1	213,2	127,2	255,9	86,3	194,6	132,2				22,9	
F											1,5	0,6	92,3		208,7
p	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	>0.05	>0.05	<0.001	<0.001	<0.001

Table 2. Comparative Mann-Whitney (U) test of mean values obtained from individuals of 174 wild populations (see Table 1) vs 6 inbred lines (data retrieved from Catalán et al. 2012) for the 15 analysed phenotypic characters in *B. distachyon*, *B. stacei* and *B. hybridum*. W- Wild populations; I- Inbred lines (means with the same letter do not differ significantly ($p<0.05$) between species after Tukey's (wild populations) and Mann-Whitney (inbred lines) pairwise comparison tests in each independent data set). Variables that do not differ significantly ($p<0.05$) between the two compared data sets (W vs I) for each character and species are underlined.

	LGCL	PGL	H	NNTC	SLL	SLW	IL	NSI	SLA	SLB	NFI	UGL	LL	AL	CL
B. distachyon															
W	**22,5**[a]	**30,4**[a]	**19,8**[a]	**4,0**[a]	**3,0**[a]	**1,7**[a]	**2,3**[a]	**2,1**[a]	**1,6**[a]	**1,1**[a]	**7,9**[a]	**6,0**[a]	**7,2**[a]	**10,7**[a]	**5,5**[a]
I	23.26 [c]	29.87 [c]	26.13 [b]	3.30 [c]	6.68 [b]	2.84 [b]	3.25 [a]	2.69 [a]	1.63 [b]	1.27 [b]	7.00 [b]	7.23 [b]	8.05 [c]	11.45 [a]	6.75 [a]
U	2820,5	3084,5	425,5	910	79	46,5	559,5	791,5	1196	441,5	832	538,5	425	918,5	110,5
p	0,07	0,61	0,03	0,82	0	0	0	0,03	0,92	0	0,12	0	0	0,12	0
B. stacei															
W	**25,2**[b]	**33,9**[b]	**43,6**[c]	**4,4**[a]	**7,4**[b]	**2,7**[c]	**5,3**[c]	**3,3**[c]	**2,2**[b]	**1,6**[b]	**8,5**[a]	**5,8**[a]	**9,4**[c]	**12,4**[c]	**6,9**[b]
I	28.22 [b]	32.58 [b]	35.56 [c]	2.94 [b]	11.06 [a]	4.15 [a]	6.12 [b]	2.75 [a]	2.29 [a]	1.61 [a]	9.24 [a]	6.24 [c]	8.91 [b]	7.27 [c]	5.68 [b]
U	3325	2903,5	236,5	333	186	171,5	423	380	901	897	806,5	691,5	758	129	165
p	0	0,94	0,06	0	0	0	0,13	0,07	0,74	0,45	0,36	0,06	0,08	0	0
B. hybridum															
W	**29,3**[c]	**38,7**[c]	**35,9**[b]	**5,7**[b]	**7,5**[b]	**2,4**[b]	**3,5**[b]	**2,7**[b]	**2,1**[b]	**1,5**[b]	**8,1**[a]	**5,9**[a]	**8,9**[b]	**11,6**[b]	**6,7**[b]
I	33.64 [a]	38.27 [a]	33.09 [a]	3.72 [a]	10.30 [a]	2.75 [b]	3.93 [a]	2.71 [a]	2.22 [a]	1.56 [a]	8.15 [ab]	7.92 [a]	10.49 [a]	9.68 [b]	7.02 [a]
U	5090	14182	1636,5	1551,5	1377,5	2025,5	2528	3619	3321	2401,5	3310,5	919,5	1452	1784,5	8781,5
p	0	0,78	0,58	0	0,01	0,06	0,04	0,9	0,81	0,03	0,79	0	0	0	0,01

Table 3. Assignment probabilities of individuals from 174 wild populations (W) and from 6 inbred lines plus 147 wild populations (I+W) of *B. distachyon*, *B. stacei* and *B. hybridum* based on discriminant analysis of 15 phenotypic traits. N, number of populations and populations + inbred lines studied.

Data sets	Samples	N	Predicted Group Membership		
			B. distachyon	***B. stacei***	***B. hybridum***
	B. distachyon	44	44 (100%)	0	0
	B. stacei	30	0	25(83,3%)	5(16,7%)
W	*B. hybridum*	100	3(3%)	5(5%)	92(92%)
	B. distachyon	46	46 (100%)	0	0
	B. stacei	31	1 (3,2%)	25(80,6%)	5 (16,1%)
I+W	*B. hybridum*	103	3 (3%)	5 (5%)	95 (92%)

Table 4. ANOVA test of 15 variables used for comparisons among wild individuals from intraspecific groups within each species (*Brachypodium distachyon, B. stacei*, *B. hybridum*). Superscripts denote Least Significant Difference (LSD) pairwise comparisons between geographic groups within species; means with the same letter do not differ significantly (p<0.05). N, number of individuals analysed. Characters with significant differences only for some comparisons: *B. distachyon*:* IL=North-East ≠ South; North-West ≠ South; Cádiz ≠ North-East + South + Center + North-West. ** NSS= North-West ≠ North-East + South; Cádiz ≠ South. *B. stacei*:* **SLL= South ≠ Balearic Islands, Israel, Iran

Species	N	LGCL	PGL	H	NNTC	SLL	SLW	IL	NSS	SLA	SLB	NFS	UGL	LL	AL	CL
B. distachyon								*	**							
North-East	23	23,2	30,1	13,8[c]	2,7[b]	2,5[c]	1,8	2,3	2,1	1,7	1,1	8,5[b]	6,5[a]	7,3	11,2[ab]	5,3
South	8	23,0	28,6	18,6[c]	5,5[a]	3,1[bc]	1,5	1,8	1,6	1,5	1,1	6,7[c]	4,3[b]	7,1	9,5[c]	5,8
Center	3	22,1	28,5	32,2[b]	7,3[a]	4,3[ab]	2,1	2,6	2,4	1,6	1,0	7,8[bc]	6,1[a]	7,0	10,0[bc]	5,0
North-West	6	21,4	30,9	42,3[a]	6,5[a]	5,5[a]	1,9	2,8	3,0	1,5	1,2	7,3[bc]	6,7[a]	7,4	10,7[bc]	5,6
Cádiz	1	21,4	34,8	36,4[ab]	4,0[ab]	2,6[bc]	1,8	4,3	3,0	2,0	1,6	12,5[a]	6,7[a]	7,6	14,0[a]	6,5
F		1,2	1,1	32,2	12,9	8,6	1,4	5,2	4,9	1,6	2,0	3,7	7,1	0,5	3,5	2,2
p		>0.05	>0.05	<0.001	<0.001	<0.001	>0.05	<0.05	<0.05	>0.05	>0.05	<0.05	<0.001	>0.05	<0.05	>0.05
B. stacei						***										
Almeria	4	26,9	33,2[b]	45,7[ab]	3,6[ab]	6,4	2,8	5,5[ab]	3,1	2,7	1,9	10,0	5,0	10,1	12,1	6,7
South	6	22,3	30,1[b]	55,9[a]	6,2[a]	9,3	2,9	6,1[a]	3,6	2,1	1,4	7,2	6,3	9,5	14,0	6,8
Canary Islands	4	25,0	31,3[b]	49,1[a]	4,0[ab]	6,1	2,4	5,3[ab]	3,5	2,1	1,4	8,6	5,8	9,2	10,5	6,8
Balearic Islands	4	27,6	36,6[b]	19,0[c]	2,8[b]	4,4	2,3	3,7[b]	2,5	2,0	1,5	9,5	5,8	8,6	11,5	6,4
Israel	6	25,7	35,8[b]	42,3[ab]	5,8[a]	5,0	2,5	5,3[ab]	3,3	2,2	1,7	8,7	6,4	10,2	15,1	6,9
Iran	3	28,5	47,2[a]	27,7[bc]	3,6[ab]	4,5	2,3	4,1[ab]	2,3	2,6	2,1	11,6	5,6	9,3	14,3	7,7
Tunisia	1	28,6	30,9[b]	42,0[abc]	4,0[ab]	4,2	1,2	5,4[ab]	3,0	2,2	1,7	10,0	5,7	7,4	11,5	6,4
Greece	1	19,7	28,6[b]	65,0[a]	5,8[ab]	11,0	2,8	6,0[ab]	4,3	1,8	0,9	7,8	5,2	10,4	14,2	6,1
F		1,8	8,1	17,0	4,6	5,4	1,4	4,1	3,7	1,7	2,0	1,9	1,0	1,9	2,0	2,3
p		>0.05	<0.001	<0.001	<0.05	<0.001	>0.05	<0.05	<0.05	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05
B. hybridum																
North Spain	7	30,3	35,5[b]	21,5[c]	2,8[c]	3,5[c]	1,8[c]	4,0[b]	2,9[abc]	2,2[b]	1,3[b]	9,9[a]	7,2[ab]	8,1[c]	12,5[ab]	6,3[bc]
Canary Islands	10	28,8	44,0[a]	45,8[a]	3,4[c]	6,6[b]	2,7[ab]	5,2[a]	3,2[ab]	2,8[a]	1,9[a]	11,1[a]	7,6[a]	10,2[ab]	11,8[bc]	7,4[a]
South Spain	23	29,5	36,4[b]	36,7[b]	6,2[a]	7,9[ab]	2,3[b]	3,3[c]	2,7[bc]	2,1[b]	1,5[b]	7,3[b]	5,4[c]	9,4[b]	11,6[bc]	6,7[b]
Balearic Islands	15	28,5	38,8[b]	18,2[c]	3,8[c]	3,5[c]	1,6[c]	2,7[d]	1,9[d]	2,1[b]	1,4[b]	9,6[a]	5,7[c]	6,7[d]	11,0[bc]	6,1[c]
Mediterranean	16	30,5	37,8[b]	46,9[a]	6,8[a]	9,1[c]	2,4[ab]	3,7[bc]	3,4[a]	2,0[b]	1,3[b]	7,5[b]	5,2[c]	7,8[c]	10,4[c]	6,6[b]
Middle East	18	28,7	38,3[b]	35,3[b]	5,2[b]	6,7[a]	2,7[a]	3,3[cd]	2,3[cd]	2,2[b]	1,5[b]	7,8[b]	6,4[b]	10,4[a]	13,6[a]	7,4[a]
F		1,2	6,0	18,5	13,7	12,1	10,0	12,2	5,5	5,2	4,7	8,0	10,1	17,2	3,9	9,5
p		>0.05	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.05	<0.001

Table 5. Pearson correlation coefficient between 435 metabolic variables (*m/z*) and 15 phenotypic traits based on 12 ecotypes of *B. distachyon*, *B. stacei* and *B. hybridum*, *, Bonferroni corrected significant p-values (< 0.05). ** many possible isomers with this particular accurate mass (see Table S9).

m/z	LGCL	PGL	H	NNTC	SLL	SLW	IL	NSS	SLA	SLB	NFS	UGL	LL	AL	CL	Putative Ionization Product	Adduct
n103.09	0.707	0.906 *	0.656	0.834	0.488	0.300	0.439	0.537	0.539	0.500	0.533	0.702	0.555	0.468	0.474	Hydroxy butyrate	[M-H]1-
n135	0.784	0.936 *	0.601	0.807	0.553	0.279	0.384	0.436	0.427	0.405	0.462	0.637	0.553	0.432	0.487	Threonate	[M-H]1-
n173.09	0.578	0.900 *	0.618	0.878	0.347	0.107	0.394	0.597	0.520	0.481	0.581	0.641	0.505	0.506	0.450	Shikimate	[M-H]1-
n174.09	0.724	0.929 *	0.617	0.885	0.429	0.101	0.345	0.533	0.444	0.405	0.488	0.633	0.497	0.437	0.519	^{13}C Isotope of Shikimate	[M-H]1-
n191.09	0.605	0.919 *	0.610	0.856	0.429	0.189	0.423	0.608	0.530	0.492	0.588	0.682	0.534	0.496	0.463	Quinate	[M-H]1-
n192.09	0.590	0.897 *	0.646	0.856	0.394	0.218	0.460	0.628	0.587	0.552	0.633	0.707	0.547	0.528	0.474	^{13}C Isotope of Quinate	[M-H]1-
n222.09	0.528	0.873	0.650	0.890 *	0.343	0.076	0.460	0.699	0.608	0.556	0.640	0.655	0.551	0.561	0.534	*N*-Acetyl tyrosine	[M-H]1-
n223.09	0.762	0.911 *	0.638	0.819	0.583	0.316	0.481	0.596	0.463	0.447	0.548	0.672	0.546	0.430	0.571	Sinapate	[M-H]1-
n236.09	0.658	0.714	0.823	0.571	0.573	0.421	0.752	0.614	0.835	0.808	0.730	0.643	0.891 *	0.768	0.690	*O*-Phospho homoserine	[M+K-2H]1-
n289.18	0.697	0.890 *	0.636	0.817	0.398	0.229	0.347	0.425	0.526	0.483	0.466	0.694	0.547	0.490	0.445	Sedoheptulose 7-phosphate	[M-H]1-
n420.18	0.472	0.632	0.811	0.571	0.539	0.661	0.866	0.780	0.874	0.876	0.891 *	0.760	0.756	0.700	0.630	β-1,4-Mannose-*N*-acetyl glucosamine	[M+K-2H]1-
n588.09	0.736	0.892 *	0.658	0.803	0.663	0.500	0.628	0.572	0.554	0.546	0.583	0.631	0.648	0.515	0.578	ADP-Glucose	[M-H]1-
n819.63	0.598	0.907 *	0.697	0.811	0.532	0.309	0.576	0.588	0.659	0.626	0.673	0.651	0.723	0.666	0.553	PG(18:1(11Z)/22:6(4Z,7Z,10Z,13Z,16Z,19Z))**	[M-H]1-
n89.09	0.666	0.869	0.521	0.892 *	0.318	0.030	0.237	0.478	0.311	0.284	0.426	0.558	0.311	0.290	0.416	Oxalate	[M-H]1-
p445.27	-0.576	-0.751	-0.607	-0.534	-0.320	-0.352	-0.480	-0.519	-0.778	-0.764	-0.601	-0.904 *	-0.749	-0.723	-0.580	Unknown	-
p796.63	0.413	0.582	0.687	0.409	0.625	0.537	0.834	0.581	0.806	0.788	0.735	0.470	0.897 *	0.768	0.536	PC(16:0/18:2(2Z,4Z))**	[M+K]1+
p815.54	0.555	0.724	0.758	0.530	0.730	0.594	0.787	0.620	0.804	0.770	0.716	0.663	0.910 *	0.746	0.633	SQDG(16:0/16:1(11Z))**	[M+Na]1+
p816.54	0.548	0.747	0.708	0.493	0.699	0.593	0.790	0.664	0.820	0.803	0.765	0.724	0.913 *	0.758	0.607	PC(18:3(8E,10E,12E)/18:3(8E,10E,12E))**	[M+K]1+
p822.54	0.593	0.688	0.741	0.493	0.647	0.531	0.801	0.589	0.813	0.798	0.737	0.590	0.900 *	0.746	0.608	PC(18:0/18:3(9Z,12Z,15Z)/0:0)**	[M+K]1+
p823.54	0.690	0.692	0.840	0.585	0.668	0.478	0.772	0.563	0.809	0.776	0.682	0.591	0.904 *	0.745	0.764	PG(18:0/20:3(5Z,8Z,11Z))**	[M+Na]1+

LEGENDS TO FIGURES

Figure 1.- Geographic distribution of *B. distachyon* (blue), *B. stacei* (red) and *B. hybridum* (purple) samples used in the phenotypic and metabolomic study. Wild populations (circle), inbred lines (square), metabolomic samples (triangle).

Figure 2.- Box and whisker plots (median, percentiles, range) of 15 morphoanatomical characters analyzed in 1050 wild (grey) and inbred (white) individuals of the three species of *B. distachyon* s. l. complex. Variables that significantly discriminate *B. distachyon* vs. *B. stacei* vs. *B. hybridum* (A); *B. distachyon* vs. *B. stacei* + *B. hybridum* (B); *B. hybridum* vs. *B. distachyon* + *B. stacei* (C); variables that do not discriminate between species (D).

Figure 3.- Two-dimensional PCA plot of 46 wild populations *of B. distachyon* (blue), 31 of *B. stacei* (red) and 103 of *B. hybridum* (purple) based on averaged values of individuals analyzed for 15 phenotypic traits (see Tables 1, S2). The first and second PCA axes explain 79.2 % and 10.4 % of the total variation, respectively.

Figure 4.- Two-dimensional DA scatterplots of populations of *B. distachyon* (blue), *B. stacei* (red) and *B. hybridum* (purple) based on averaged values of individuals analyzed for 15 phenotypic traits in 174 wild populations (A) and in 174 wild populations plus 6 inbred lines (B). Wild populations (circles), inbred lines (stars), accessions with metabolites (*B. distachyon* diamonds; *B. stacei* triangle; *B. hybridum* squares).

Figure 5.- Two-dimensional DA scatterplots of 41 Spanish populations of *B. distachyon* (A), 29 circum-Mediterranean populations of *B. stacei* (B) and 89 circum-Mediterranean

populations of *B. hybridum* (C) based on averaged values of wild individuals analyzed for 15 phenotypic traits. Colors for the respective geographic groups of each species are indicated in the charts.

Figure 6.- Box- and whisker plots (median, percentiles, range) of a subsample of 16 significantly discriminant metabolomic traits analyzed in 5 ecotypes (60 replicates) of *B. distachyon* (blue), 3 (36) of *B. stacei* (red), and 4 (48) of *B. hybridum* (purple). (A) Positive mode metabolites; (B) Negative mode metabolites.
Assignment of metabolomics signals to putative ionization products is indicated for each trait.

Figure 7.- Two-dimensional DA scatterplot of 5 ecotypes (60 replicates) of *B. distachyon* (circles), 3 (36) of *B. stacei* (triangles) and 4 (48) of *B. hybridum* (squares) based on averaged values of individuals analyzed for 434 metabolomic traits. Colors for each ecotype are indicated in the charts.

SUPPLEMENTAL MATERIAL

Table S1. Sources of *B. distachyon*, *B. stacei* and *B. hybridum* individuals from wild populations and inbred lines (*) included in the phenotypic and metabolomic study. Double asterisks (**) indicate individuals used in both types of analyses, in the remaining cases the individuals were used only in the phenotypic analysis. Diamonds indicate *B. distachyon*, *B. stacei* and *B. hybridum* type samples. Measurements of phenotypic variables correspond to averaged values from up to 10 individuals per population (and up to 5 measurements per trait and individual). The geographic origins and nature of all the studied samples are indicated [wild (W), herbaria (H), seed bank (S) or inbred (I) plants]. For abbreviation of variables see text and Table S2.

Table S2. Morphological variables used in the phenotypic analysis. Results of the Kolmogorov-Smirnov normality test. Significance: ***: $p<0.001$; **: $p<0.01$; *: $p<0.5$; n. s.: non-significant.

Table S3. Pairwise Spearman correlation coefficients between phenotypic traits (averaged values) analyzed in wild individuals of *B. distachyon*, *B. stacei* and *B. hybridum*. Significant correlation values ($p<0.001$) are highlighted in bold.

Table S4. Loadings of phenotypic traits onto the first PCA components. Highest contributions of characters to each component are highlighted in bold.

Table S5. Contribution of phenotypic variables to the first canonical discriminant functions obtained for the two data sets of individuals of *B. distachyon*. *B. stacei* and *B. hybridum* analyzed: W (174 wild populations data set). I + W (6 inbred lines + 174 wild populations data set). Variables that contributed more to the functions are highlighted in bold.

Table S6. Contribution of phenotypic variables to the first canonical discriminant functions obtained for individuals from 41 wild populations of *B. distachyon*. Variables that contribute more to the functions are highlighted in bold.

Table S7. Contribution of phenotypic variables to the first canonical discriminant functions obtained for individuals from 29 wild populations of *B. stacei*. Variables that contribute more to the functions are highlighted in bold.

Table S8. Contribution of phenotypic variables to the first canonical discriminant functions obtained for individuals from 89 wild populations of *B. hybridum*. Variables that contribute more to the functions are highlighted in bold.

Table S9. Annotation of 434 'explanatory' nominal mass fingerprint signals by targeted accurate *m/z* data analysis and MZedDB database search at MSI level of identification 2. The *m/z* signal with duplicate annotations, i.e., other adducts or isotopes of same metabolite, are indicated as plain (un-bold) text.

Table S10. List of annotated *m/z* signals where signal identities were confirmed by comparing MS^n fragmentation pattern with that of standard's.

Table S11. Contribution of metabolomic variables to the first canonical discriminant functions obtained for the studied ecotypes of *B. distachyon* (5 ecotypes, 60 replicates), *B.*

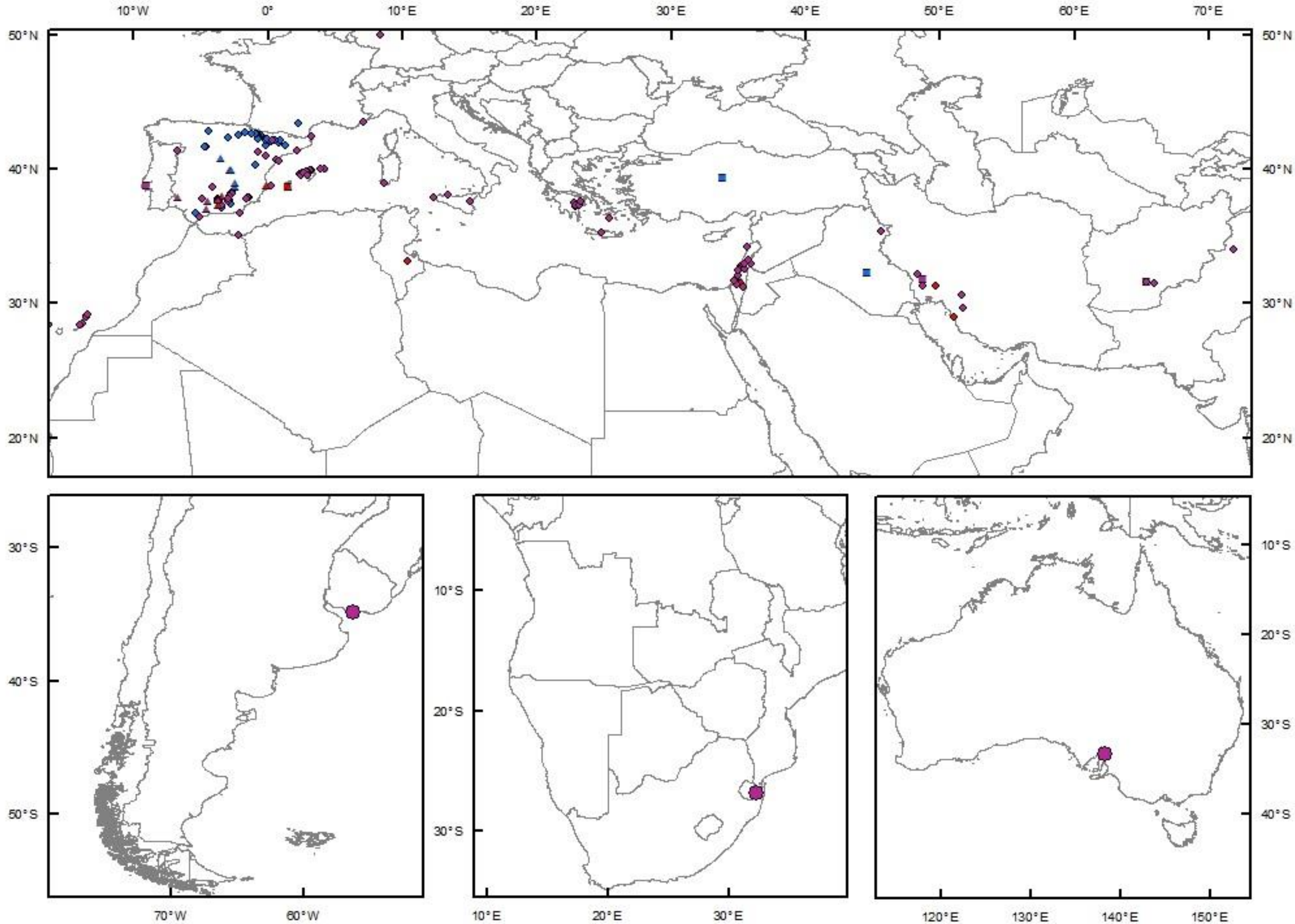
stacei (3, 36) and *B. hybridum* (4, 48). Contribution values of positive and negative metabolites to the functions. (a) Metabolites not included in the discriminant analysis (see Figure 7). (b) Duplicate *m/z* signals with same metabolite annotations not included in the discriminant analysis (see Figure S1). * $p<0.05$.

Table S12. Statistics of 16 metabolites and significance tests of their mean values in *Brachypodium distachyon*, *B. stacei* and *B. hybridum*. N, number of ecotypic samples analysed. ANOVA (F; d.f. 2) test of variables used for comparisons among species. Superscripts denote Tukey pairwise comparisons between species; means with the same letter do not differ significantly ($p<0.05$).

Figure S1. Two-dimensional DA scatterplot of 5 ecotypes (60 replicates) of *B. distachyon* (circles), 3 (36) of *B. stacei* (triangles) and 4 (48) of *B. hybridum* (squares) based on averaged values of individuals analyzed for 282 metabolomic traits (when *m/z* signals of same annotations showing different adducts were discarded from analysis; see Tables S9 and S11). Colors for each ecotype are indicated in the charts.

Figure S2. Tentative identification of main lipid in positive ion mode mass bin *m/z* 815.54 by MS^2 fragmentation analysis.

Fig. 1



10°W
0°
10°E
20°E
30°E
40°E
50°E
60°E
70°E
50°N
40°N
30°N
20°N
30°S
40°S
50°S
70°W
60°W
10°S
20°S
30°S
10°E
20°E
30°E
10°S
20°S
30°S
40°S
120°E
130°E
140°E
150°E

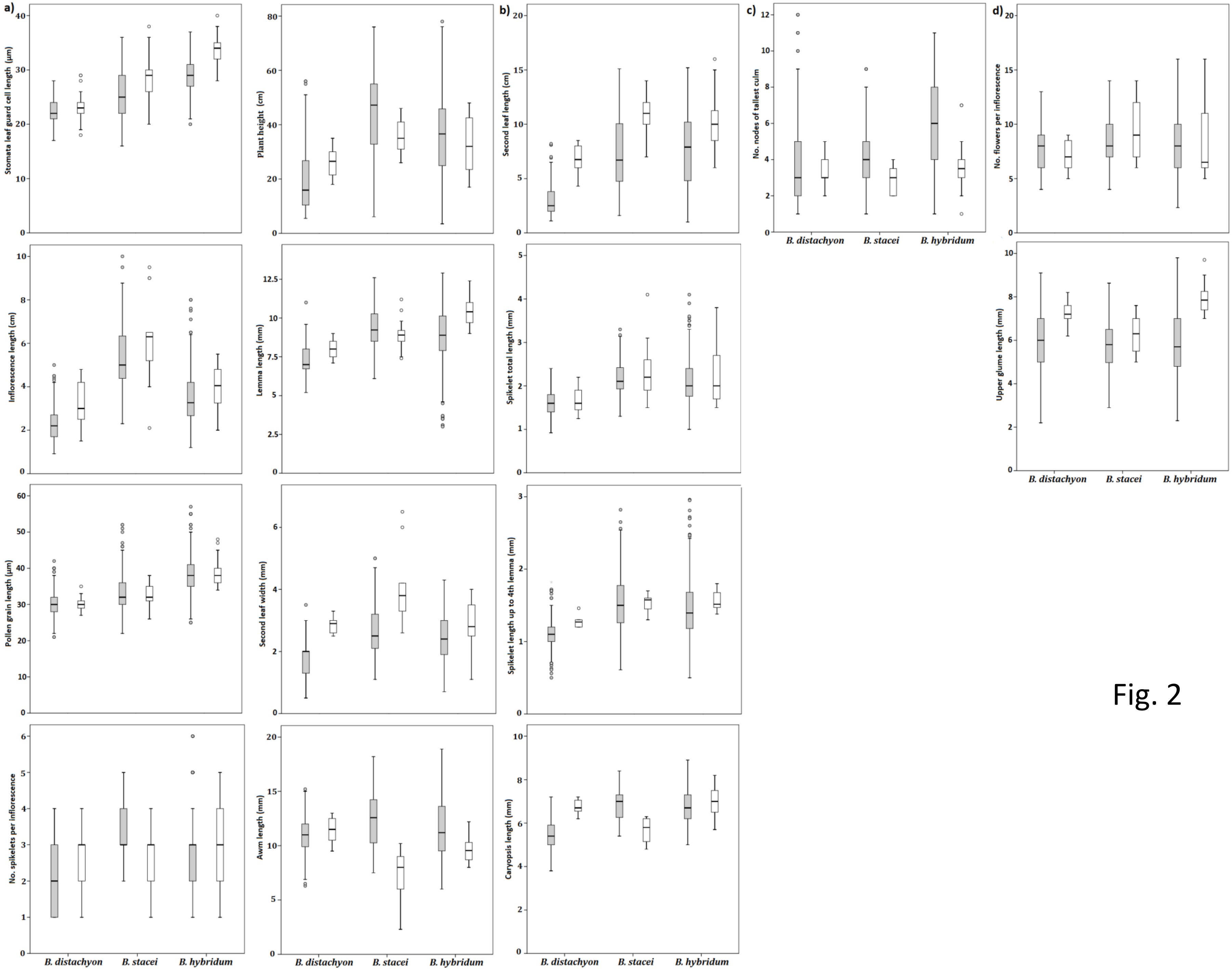
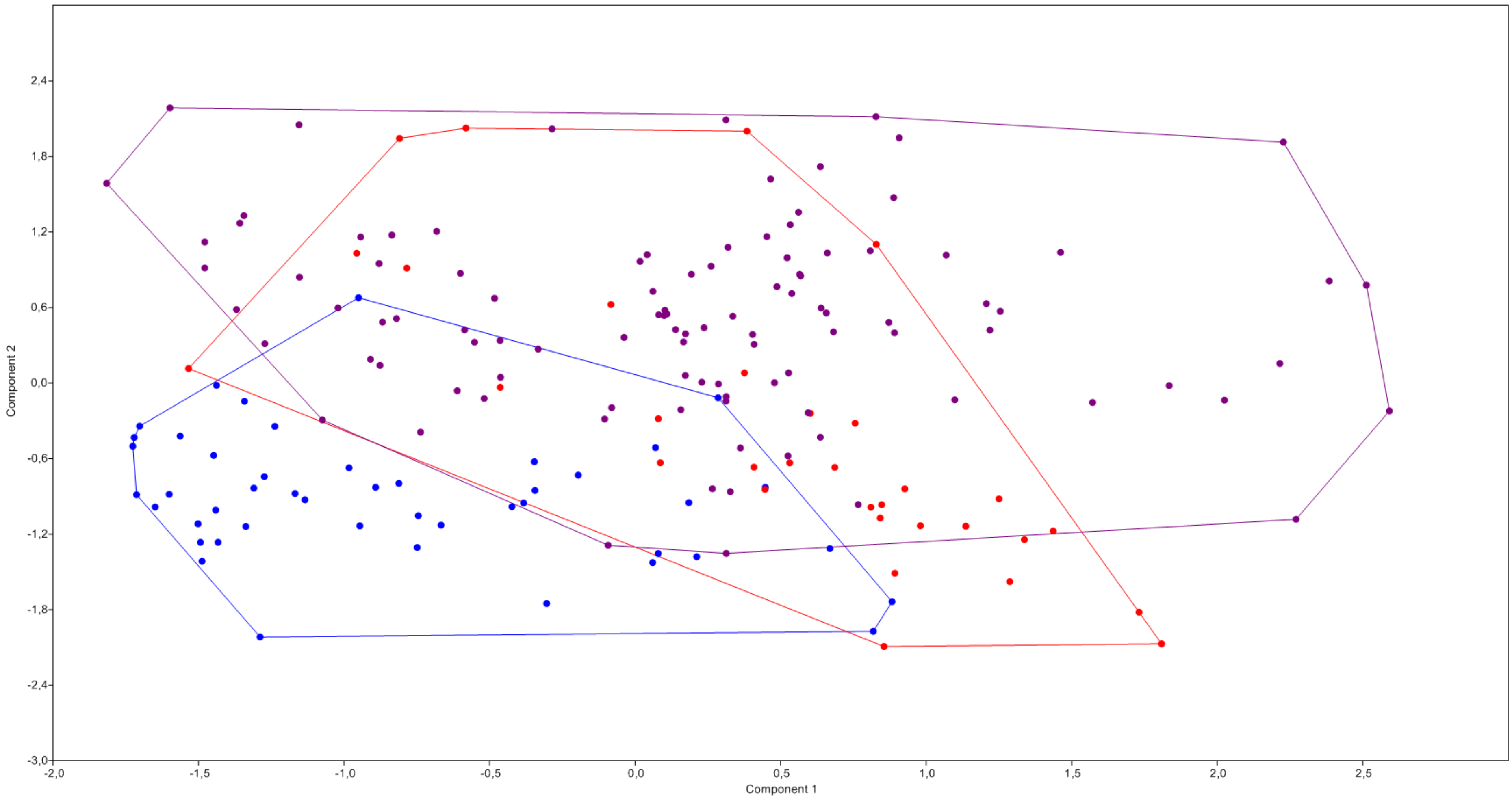

a)
b)
c)
d)
Stomata leaf guard cell length (µm)
Plant height (cm)
Second leaf length (cm)
No. nodes of tallest culm
No. flowers per inflorescence
Inflorescence length (cm)
Lemma length (mm)
Spikelet total length (mm)
Upper glume length (mm)
Pollen grain length (µm)
Second leaf width (mm)
Spikelet length up to 4th lemma (mm)
No. spikelets per inflorescence
Awn length (mm)
Caryopsis length (mm)
B. distachyon
B. stacei
B. hybridum

Fig. 2

Fig. 3



2,4
1,8
1,2
0,6
0,0
-0,6
-1,2
-1,8
-2,4
-3,0
Component 2
-2,0
-1,5
-1,0
-0,5
0,0
0,5
1,0
1,5
2,0
2,5
Component 1

Fig. 4

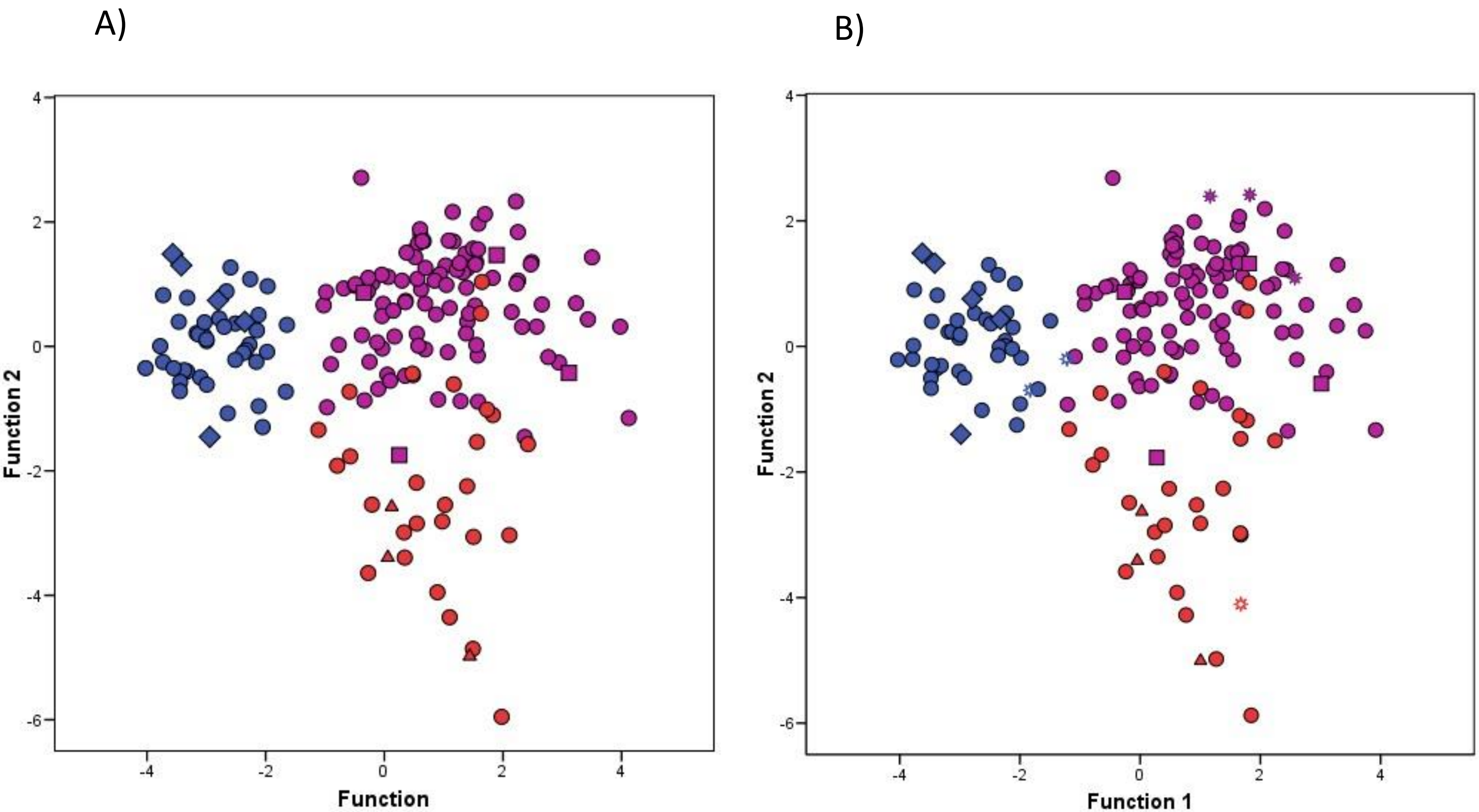
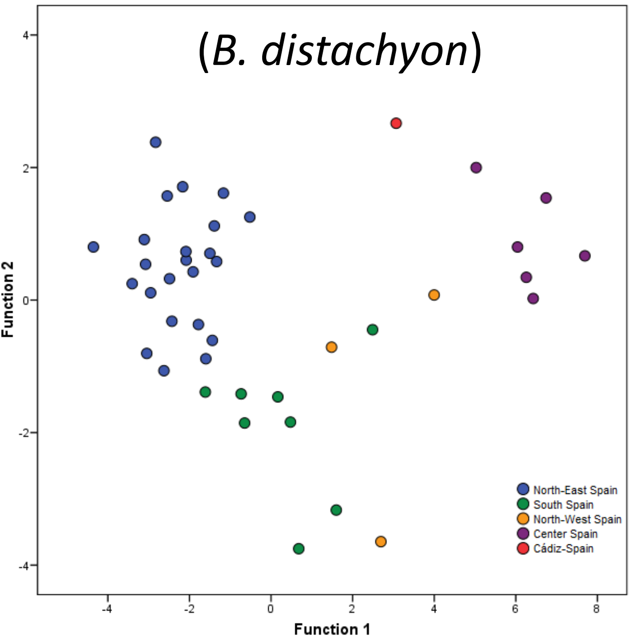
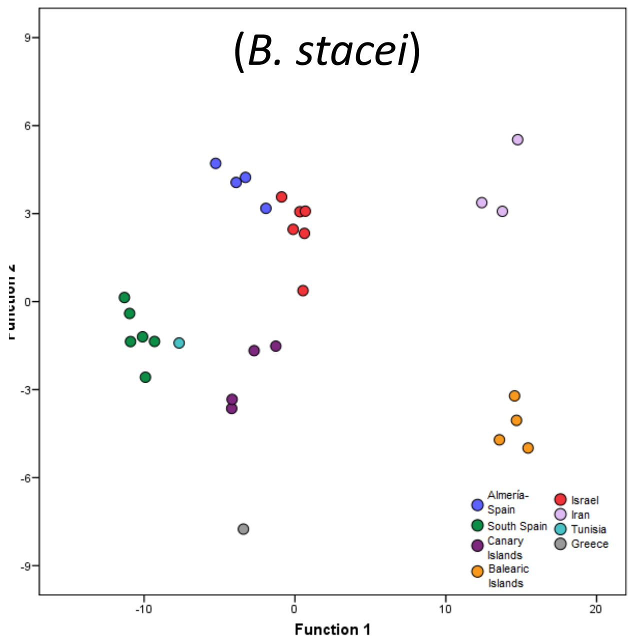


Fig. 5

A)


(B. distachyon)
Function 2
Function 1
North-East Spain
South Spain
North-West Spain
Center Spain
Cádiz-Spain

B)


(B. stacei)
Function 1
Almería-Spain
South Spain
Canary Islands
Balearic Islands
Israel
Iran
Tunisia
Greece

C)

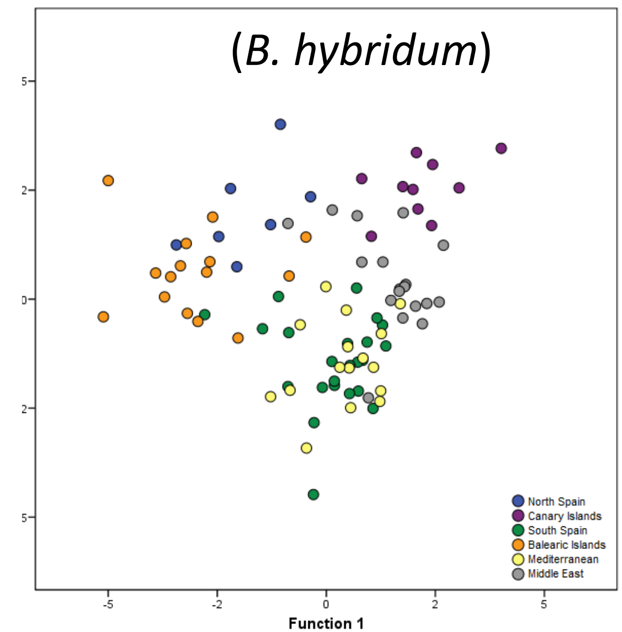
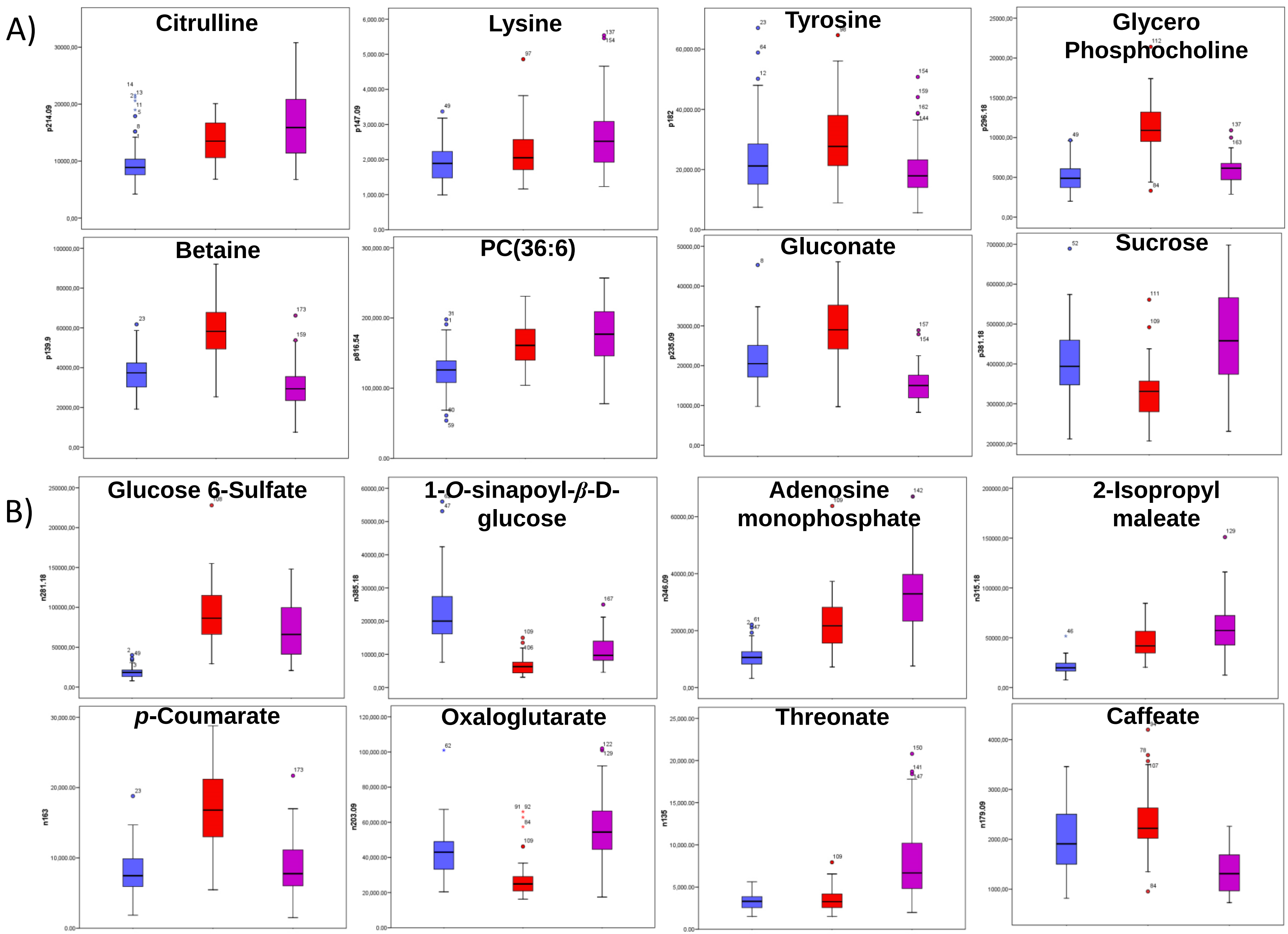
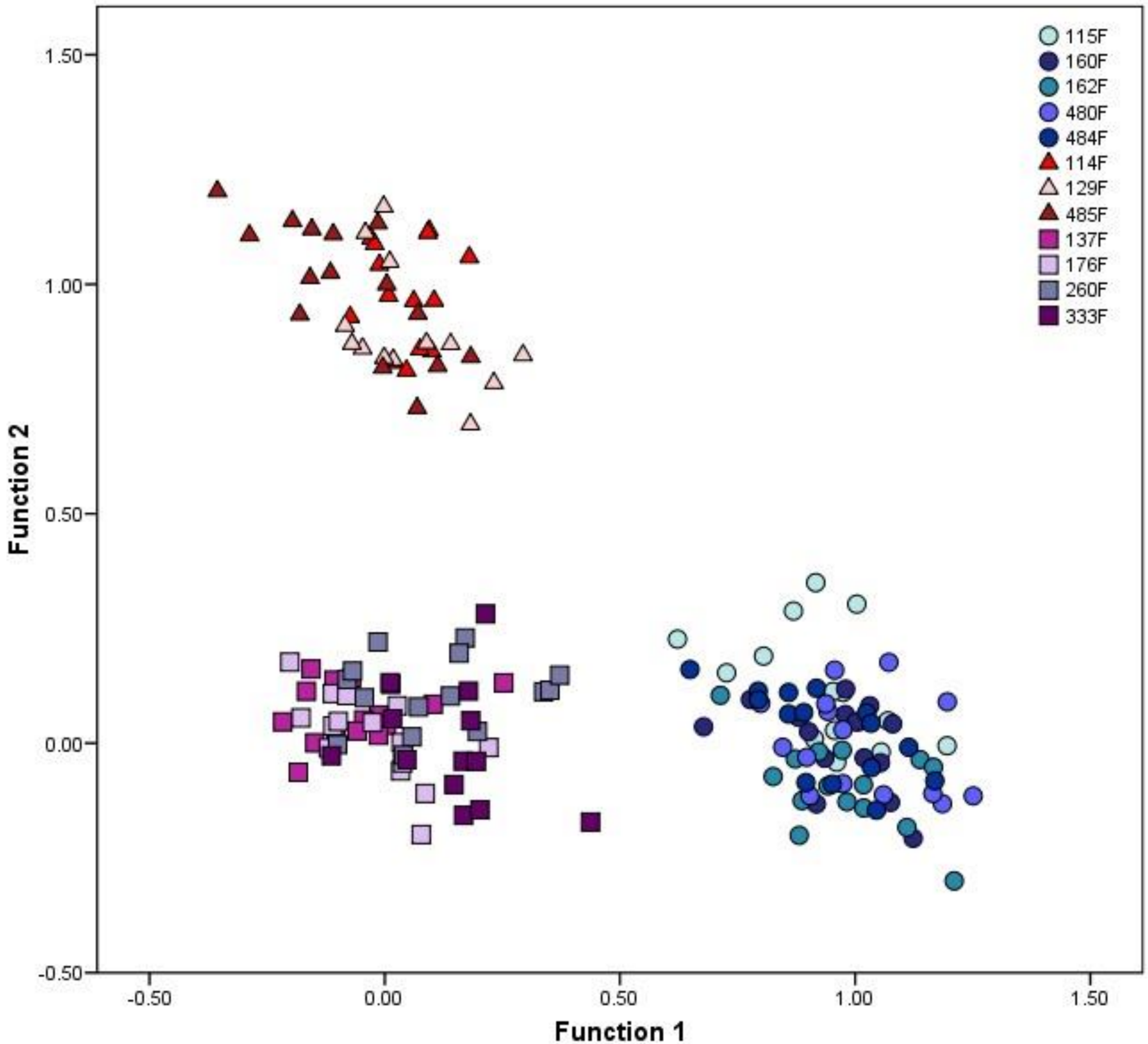

(B. hybridum)
Function 1
North Spain
Canary Islands
South Spain
Balearic Islands
Mediterranean
Middle East

Fig. 6



A)
Citrulline
Lysine
Tyrosine
Glycero Phosphocholine
Betaine
PC(36:6)
Gluconate
Sucrose
B)
Glucose 6-Sulfate
1-O-sinapoyl-β-D-glucose
Adenosine monophosphate
2-Isopropyl maleate
p-Coumarate
Oxaloglutarate
Threonate
Caffeate

Fig. 7



115F
160F
162F
480F
484F
114F
129F
485F
137F
176F
260F
333F
1.50
1.00
0.50
0.00
-0.50
Function 2
-0.50
0.00
0.50
1.00
1.50
Function 1

Table S1. Sources of *B. distachyon*, *B. stacei* and *B. hybridum* individuals from wild populations and inbred lines (*) included in the phenotypic and metabolomic study. Double asterisks (**) indicate individuals used in both types of analyses, in the remaining cases the individuals were used only in the phenotypic analysis. Diamonds indicate *B. distachyon*, *B. stacei* and *B. hybridum* type samples. Measurements of phenotypic variables correspond to averaged values from up to 10 individuals per population (and up to 5 measurements per trait and individual). The geographic origins and nature of all the studied samples are indicated [wild (W), herbaria (H), seed bank (S) or inbred (I) plants]. For abbreviation of variables see text and Table S2.

Specie	Locality	LGCL	PGL	H	NNTC	SLL	SLW	IL	NSS	SLA	SLB	NFS	UGL	LL	AL	CL
B. distachyon *◊	Iraq: Bd21 USDA genome sequenced (type) (H)	22,3	30	28	3	6,3	2,9	3	2,5	1,7	1,3	7,1	7	8	12	7
B. distachyon	France: Aude. USDA:W619177 (S)	22,8	33	32	6,6	3,5	0,9	2	1,8	1,5	1	6,3	3,9	6,6	7,9	5
B. distachyon	Israel: Julis. AB&SE:BRA65 (S)	21,4	30	47	6	4,3	3,5	4	3	2,4	1,8	13	7	8,7	13	5
B. distachyon	Spain: Albacete, Alcaraz. CS:Bd115F** (I)	20,8	29	50	6,6	5,6	1,8	3	3,5	1,8	1,3	6,4	7,4	8,1	11	6
B. distachyon	Spain: Albacete, Bonillo. CS:Bd160F** (I)	21,4	30	39	5,7	4,8	2	3	3	1,7	1,4	8	8	7,9	11	6
B. distachyon	Spain: Cádiz,Grazalema. AM:Graz (S)	21,4	35	36	4	2,6	1,8	4	3	2	1,6	13	6,7	7,6	14	7
B. distachyon	Spain: Cuenca, Sedóbriga. CS:Bd162F** (I)	21,3	33	38	7	3,5	1,8	3	3	1,7	1,4	6,5	7,5	8,4	13	6
B. distachyon	Spain: Cuenca. CS:Bd484F** (I)	20	30	37	7,3	5,8	1,6	2	2,7	1,4	1	6	6,4	7,1	9,8	6
B. distachyon	Spain: Escaray, Zorraquín, monte Turgaiza.HS:100198-1 (S)	24,8	36	40	5,3	8,1	2,3	2	2,8	1,4	0,9	10	4,4	6,1	7,5	5
B. distachyon	Spain:Granada, Sierra Huetor, Puerto de la Mora. PC:B111 (W)	22	31	15	4	1,5	0,9	1	1	1,2	0,9	6	4,1	6,2	8,9	6
B. distachyon	Spain: Granada, Sierra de Baza, Mirador de Narvaez1. PC Bsta128 (W)	24,4	28	24	10,8	5,3	2,2	2	1,2	1,5	1	5,6	3,6	6,9	10	5
B. distachyon	Spain: Granada, Sierra de Baza, Mirador de Narvaez 2. PC:B129 (W)	21,3	28	14	2,7	1,9	1,6	3	2,7	1,8	1,4	9,7	4,9	7	8,4	6
B. distachyon	Spain: Granada, Sra Nevada, Ctra al Veleta, ca. Restaurante Las Viboras. PC:B136 (W)	26	27	9,3	3,7	1,6	1,1	2	1	1,6	1,2	7,3	3,4	7,4	12	6
B. distachyon	Spain: Huesca, Jaca, Banaguas. PC&LM:B12 (W)	19,2	30	24	3,2	3,3	2,3	2	3,3	1,5	1,2	6,6	5,8	6,3	11	5
B. distachyon	Spain: Huesca, Puente de la Reina. PC&LM:B14 (W)	21,4	26	11	2,4	2,8	2	3	2,6	1,9	1,2	10	7	8	11	5
B. distachyon	Spain: Huesca, Arens. PC&LM:B18 (W)	27	27	14	2	2,5	2	3	2,4	1,8	1	9,2	7,2	6,6	11	5
B. distachyon	Spain: Huesca, Adahuesca, San Jerónimo. PC&LM:B19 (W)	24	29	17	2	2,4	2	3	2,5	1,9	1,2	9,5	6,5	7,3	13	5
B. distachyon	Spain: Huesca, Barbastro. PC&LM:B20 (W)	21,8	32	30	4,2	4,2	2,3	3	2,6	1,9	1,1	8,8	7,6	8,5	13	5
B. distachyon	Spain: Huesca, Abizanda. PC&LM:B21 (W)	26,3	30	19	2,4	2,7	2	3	2	1,7	1,2	8	6,2	7,4	13	6
B. distachyon	Spain: Huesca, Berdun. PC&LM:B22(W)	25	29	16	2,7	2,8	2	2	2,6	1,5	1	7,7	6,2	6,8	11	5
B. distachyon	Spain: Huesca, Bierge. PC&LM:B09 (W)	21	32	12	3,2	1,8	1,4	2	1,4	1,4	0,9	6,6	4,9	7,2	11	5
B. distachyon	Spain: Huesca, Alquezar. PC&LM:B11 (W)	21,5	41	19	3,2	2,6	1,9	3	1,8	2,1	1,6	11	8,5	7,3	14	6

B. distachyon	Spain: Huesca, Benabarre. PC&LM:B17 (W)	22,5	35	13	3,5	2,9	1,8	2	2,8	1,4	0,8	6,8	7,2	7,1	11	6
B. distachyon	Spain: Huesca, Sariñena. PC&LM:B05 (W)	22,4	32	7,4	2	1,5	1,6	2	2,2	1,7	1,1	9,6	6,8	7,6	8,2	5
B. distachyon	Spain: Huesca, San Miguel de Foces. PC&LM:B06 (W)	21,8	35	11	3	1,8	1,8	2	2,2	1,8	1,3	10	6	6,6	10	5
B. distachyon	Spain: Huesca, Yaso. PC&LM:B08 (W)	22,4	33	15	4,5	2,8	1,7	3	2	1,6	1,3	8,5	6	6,8	11	7
B. distachyon	Spain: Jaen, Sierra Sepura, Cortijos Nuevos, El Contadero. PC B115 (W)	21,2	29	20	9,2	3,6	1,4	2	1,2	1,4	0,9	4,6	4,2	7	8,1	6
B. distachyon	Spain: Jaen, Sierra Sepura, Cortijos Nuevos, El Contadero. PC:B116 (W)	23,8	31	22	5,8	4	2	2	1,4	1,3	0,8	5	4,5	6,8	9,4	6
B. distachyon	Spain: Jaén, Sra de Jaen, zona de pitillos. PC:B134 (W)	24,4	32	30	4,2	4,8	1,8	2	2,2	1,5	1	6,4	4,6	7,4	9,1	6
B. distachyon	Spain: Jaén, Sra de Jaen, Puerto de Navalayegua. PC:B135 (W)	20,7	22	15	3,3	2,1	1,5	3	2,3	1,9	1,3	9,3	5,3	8,4	10	7
B. distachyon	Spain: Teruel, La Puebla de Valverde, Pto del Escandón. PC:B142 (W)	23,3	31	7	2,8	2	1,6	2	2,3	1,7	1,3	9,8	3,4	7,5	8,3	6
B. distachyon	Spain: Lleida, Fondedou . PC&LM:B30 (W)	21,5	29	7,5	2,3	2,1	1	2	2	1,4	1	7,3	6,5	6,8	11	4
B. distachyon	Spain: Lleida, Castillo de Mur. PC&LM:B31 (W)	24,6	28	23	2,8	4,3	2,7	3	3	1,8	1,1	9,6	7,4	7,8	13	5
B. distachyon	Spain: Lleida, Les Pallagues. PC&LM:B32 (W)	25	26	11	2	2,1	1,5	2	1,4	1,6	1,1	9	6,8	7,3	12	5
B. distachyon	Spain: Madrid. CS:Bd480F** (I)	20,4	27	50	7	5,1	2,1	4	3	1,4	1,1	7	6,3	7,1	11	6
B. distachyon	Spain: Navarra, Puerto del Perdon. PC&LM:B27 (W)	23,4	32	9,7	2,2	1,9	1,4	2	1,5	1,5	1	8,2	5,8	6,8	11	5
B. distachyon	Spain: Navarra, Los Arcos. PC&LM:B28 (W)	25,2	27	8,5	2,8	2	2	2	1,8	1,7	1,1	8,6	6,8	8,2	11	5
B. distachyon	Spain: Navarra, Puerto del Perdon. PC&LM:B27 (W)	23,4	32	9,7	2,2	1,9	1,4	2	1,5	1,5	1	8,2	5,8	6,8	11	5
B. distachyon	Spain : Otero, Valladolid. INRA-V:Abrc7d (S)	25	30	29	9,8	3,8	1,8	2	1	1,5	1	4,6	4,4	7,5	9,2	6
B. distachyon	Spain: Palencia, Cervera. AM:Cer (S)	19,8	30	37	6	2,3	1,8	4	3,3	2	1,4	12	7,3	7,1	11	5
B. distachyon	Spain: Valladolid,Renedo de Esgueva. HS:113171-1 (S)	21,6	26	31	6	6,9	2,7	2	3	1,4	0,7	7	6,5	6,4	9,4	4
B. distachyon	Spain: Zaragoza, Miramont. PC&LM:B23 (W)	24,2	26	11	3	1,5	1	2	1,1	1,4	1,1	5,8	6	6,7	11	5
B. distachyon	Spain: Zaragoza, Sigüés. PC&LM:B24 (W)	23,4	26	12	2,6	1,9	1,8	2	2,1	1,7	0,9	8,6	6,4	7,1	10	6
B. distachyon	Spain: Zaragoza, Murillo de Gallego. PC&LM:B15 (W)	24,6	30	6,9	1,3	2,3	2	2	2,2	1,8	1	9	7,3	8,2	11	5
B. distachyon	Turkey: Kiresehir, Kaman. ABR1* (I)	24,6	29	20	4,5	8,3	2,8	4	3,3	1,6	1,3	6,7	8	8,3	9,9	7
B. distachyon	Spain (S)	19,2	35	43	4,7	2,5	1,4	4	2,7	2	1,3	8,7	6,9	8,9	12	6

Specie	**Locality**	**LGCL**	**PGL**	**H**	**NNTC**	**SLL**	**SLW**	**IL**	**NSS**	**SLA**	**SLB**	**NFS**	**UGL**	**LL**	**AL**	**CL**
*B. stacei**◊	Spain: Balearic isles: Formentera. ABR114* (type) (I)	28,2	33	36	2,9	11	4,2	6	2,8	2,3	1,6	9,2	6,2	8,9	7,3	6
B. stacei	Greece: Pelopponesos, Tyros. PC:G15 (W)	19,7	29	65	5,8	11	2,8	6	4,3	1,8	0,9	7,8	5,2	10	14	6
B. stacei	Iran: Asalooyeh to Booshehr MRR:BdisIran1 (H)	30	45	20	3,3	3,5	1,8	4	2	2,7	2,4	13	5,1	9,3	13	8

B. stacei	Iran: 25 Km to Ramhorm from Ahwaz. MRR:BdisIran2 (H)	28,3	47	24	3	4,4	3,3	5	3	2,5	1,9	11	6	8,4	14	8
B. stacei	Iran: Fars, Kazeroon, Davan. MRR:B100-H141 (H)	27,3	49	39	4,7	5,7	1,8	3	2	2,7	2	11	5,6	10	17	8
B. stacei	Israel: Amazyia. AB&SE:BRA52 (S)	23,8	31	49	5	6	2,4	6	4	2,6	1,8	9	6,3	12	15	7
B. stacei	Israel: Lakhish. AB&SE:BRA135 (S)	32,7	28	36	4	6,1	2,8	7	4	1,3	1,2	8	6,1	9,9	14	6
B. stacei	Israel: Hawalid. AB&SE:BRA158 (S)	21,2	34	42	7	3,4	2,3	5	3	2,1	1,7	7	7,2	11	13	7
B. stacei	Israel: Bat Shelomo. AB&SE:BRA191 (S)	27	40	33	6	3,3	2	5	3	1,9	1,1	6	5,8	8,6	15	7
B. stacei	Israel: Yiftah. AB&SE:BRA286 (S)	28,4	43	47	9	3,6	3	5	3	3,3	2,5	14	7,1	9	16	7
B. stacei	Israel: Ziff junction. AB&SE:BRA89 (S)	21	38	47	4	7,9	2,7	5	3	2,1	1,7	8	5,7	10	18	7
B. stacei	Spain: Alicante, Xávea, Cabo La Nao. PC:B102 (W)	17,1	32	56	5,3	12	3,1	7	3,9	2	1,1	5,6	6,1	8,9	12	7
B. stacei	Spain: Alicante, Cabo de La Nao. CS:Bd483F** (I)	23,3	31	57	6,3	9,9	3,9	7	3,7	2,3	1,9	9,3	8,3	9,7	13	6
B. stacei	Spain: Almería, Cabo de Gata. EB:AL1 (S)	24	31	54	4,5	6,4	3,4	7	4	2,8	2,2	12	4,7	10	16	8
B. stacei	Spain: Almería, Cabo de Gata. EB:AL5 (S)	21,5	38	45	4	5,1	2,3	5	2,5	2,9	2,4	12	5	9,1	13	7
B. stacei	Spain: Almeria, Cabo de Gata, Playa de Genoveses. PC B108 (W)	30,5	30	44	2,8	5,9	2,8	5	3,3	2,5	1,6	8,4	5,2	11	9,3	6
B. stacei	Spain: Almeria, Cabo de Gata, Playa de Monsal. PC B109 (W)	31,6	34	41	3,2	8,4	2,6	5	2,8	2,4	1,5	8,1	5,2	10	10	6
B. stacei	Spain: Canarias: Gomera, Agulo. INIA-CRF: NC050363 (W)	26,5	33	46	4	7,8	2,7	5	4	1,9	1,2	7,3	5,3	9,4	14	7
B. stacei	Spain: Canarias: Gomera, Agulo. INIA-CRF:BGE044241 (W)	21,8	30	50	4,5	5,1	2,4	5	2,5	2,4	1,6	8	7,8	10	11	6
B. stacei	Spain: Canarias: Lanzarote, Teguise. INIA-CRF:NC050440 (S)	25	31	49	4,7	7,6	2,2	6	4	2,2	1,6	10	4,3	7,9	9,1	7
B. stacei	Spain: Canarias: Lanzarote, Teguise. INIA-CRF:BGE044249 (S)	26,8	32	51	3	4	2,5	6	3,5	2,1	1,4	9	5,8	9,1	8,7	7
B. stacei	Spain: Granada, Moclín. CS:Bd129F**(I)	20,2	30	64	6,8	7,6	2,2	6	3,4	2,4	1,9	9,4	7,2	11	16	8
B. stacei	Spain:Jaen, Sierra Cazorla, Ctra de Cortijos Nuevos a Cazorla. PC:B117 (W)	22	25	49	5	11	3,2	6	3,6	2	1,3	5,2	5,2	9,8	14	7
B. stacei	Spain: Jaen, Baeza. CS:Bd114F** (I)	24,9	31	51	6,7	7,4	2,2	6	3,3	1,9	1,5	7,7	6,5	8,9	12	6
B. stacei	Spain: Jaen, Sierra de Quesada. Tiscar. JD:18_1 (S)	26,5	31	59	7,5	7,3	2,6	5	3,5	1,8	0,9	6	4,9	9	18	7
B. stacei	Spain: Mallorca, Sa Dragonera, Gambes. DL&PC:B891 (W)	27,9	33	9,7	1,8	2,8	1,5	4	3	1,9	1,3	9	4,8	7,6	8,9	6
B. stacei	Spain:Mallorca, Bahyalbufear, Mirador Ses Animes. DL&PC:B921 (W)	29	39	21	4	4,7	2,2	4	2,5	2,2	1,7	11	6,7	8,6	14	7
B. stacei	Spain: Mallorca, Alcudia, c. Punta Negra. DL&PC:B621 (W)	28,6	40	18	2,7	4,8	2,7	3	2,3	2	1,3	8,7	5,4	8,2	10	6
B. stacei	Spain: Mallorca, Campanet, Coves. DL&PC:B771 (W)	24,8	35	27	2,8	5,2	3	4	2,3	2,2	1,6	10	6,2	10	13	6
B. stacei	Spain: Mallorca, La Victoria. INRA:13498BGVA_Esp0 (W)	27,6	31	55	3,4	12	4,1	5	3,2	1,9	1,3	6	5,3	9,1	9,6	8

Specie	Locality	LGCL	PGL	H	NNTC	SLL	SLW	IL	NSS	SLA	SLB	NFS	UGL	LL	AL	CL
B. stacei	Tunisia: Gouv. De Medénine:Ksar Hadada (NW Lfoum Tataouine). Hmünchen:67243 (H)	28,6	31	42	4	4,2	1,2	5	3	2,2	1,7	10	5,7	7,4	12	6
Specie	**Locality**	**LGCL**	**PGL**	**H**	**NNTC**	**SLL**	**SLW**	**IL**	**NSS**	**SLA**	**SLB**	**NFS**	**UGL**	**LL**	**AL**	**CL**
*B. hybridum**◊	Portugal: Lisboa, ABR113. (type)* (I)	34	36	48	7	13	2,6	4	4,5	1,5	1,5	6	8,8	10	12	7
B. hybridum	Afghanistan: Hauz-i-Mabat, Kandahar. USDA:PI219965 (S)	29,6	37	38	4,2	8	2,3	3	2,4	1,9	1,2	7,6	5,4	11	14	8
B. hybridum	Afghanistan: 35 miles from Kandahar to Kahakai dam, 4,800 ft. USDA:PL219971 (S)	33,5	36	35	5,3	9,8	3,2	3	2,3	2	1,4	6,5	5,5	11	13	8
B. hybridum	Afghanistan: USDA PI219965, ABR117* (I)	34,1	38	22	4	7,5	1,5	3	1,4	2,3	1,6	8,8	7,7	10	9,2	7
B. hybridum	Australia: Crystal Brook, 3 km upstream from town. USDA:PL533015 (S)	32,6	38	35	8	10	3,2	3	2,4	1,9	1,3	6,6	4,6	8,4	9,1	7
B. hybridum	Crete. INRA:Cre0 (S)	32,6	36	78	4	4,4	1,7	5	3,3	3,4	2,5	13	6,8	8,6	9,9	9
B. hybridum	Crete. INRA-V:Cre-1a(S)	36	36	48	7,2	12	3	3	3,8	1,7	1,1	5,5	5,8	9,6	9,2	7
B. hybridum	Crete. INRA-V:Cre-1b (S)	33,2	42	42	7,4	11	3,3	3	3,5	1,6	1	5,5	4,9	8,8	8,4	6
B. hybridum	Cerdeña: Cagliari. HMünchen:55806 (H)	27,1	39	68	5	7,5	1,8	5	4,5	1,9	1,4	9,5	5,2	6,9	11	6
B. hybridum	France: Île sainte Marguerite. INRA-V:Mar-1 (S)	30	37	36	9,4	11	2,9	3	2,8	1,6	1,1	5,2	5,1	8,4	11	7
B. hybridum	Germany. USDA:PL422452 (S)	29,8	42	42	8,6	9,3	3,1	3	2	1,8	1,3	6,2	5,3	8,9	8	6
B. hybridum	Grece: Kreta, Metohi. HMünchen:201179 (H)	30,7	40	54	5	7,6	2,1	5	3,5	1,8	1,4	8,3	6	7,8	12	8
B. hybridum	Greece: Pelopponesos: Xiropigado.PC:G12 (W)	30,4	35	53	7,5	8,3	2,4	5	5,5	1,6	0,8	6	5,6	6,7	10	7
B. hybridum	Greece: Pelopponesos: Korakovouni, Aghios Andreas.PC:G13 (W)	27,4	40	54	5,5	9,7	2,4	5	5,5	2,7	1,5	12	4,9	7,4	11	7
B. hybridum	Greece: Pelopponesos: Tyros.PC:G14 (W)	34,1	38	55	7	9,5	2,6	5	5,5	1,9	0,9	7,5	4,1	6,9	11	6
B. hybridum	Greece: Pelopponesos: Kosta1. PC:G3 (W)	29,3	39	45	7	12	2,4	3	3,7	1,4	0,9	6	4,5	5,9	10	6
B. hybridum	Greece: Pelopponesos: Ano Fanari.PC:G8 (W)	27,3	39	41	7	5,5	1,7	4	2	2,2	1,7	11	5,9	8,6	10	6
B. hybridum	Iran: Fars, Kazerun , 12 miles E of Kazerum, 3,800 ft. USDA:PL226629 (S)	33,5	41	47	4,3	8,9	2,8	4	3	2,4	1,8	9,5	5,6	11	15	7
B. hybridum	Iran: Juzestan, between Ahwaz and Shushtar, near Abe-e Gonji. USDA:PL227011 (S)	28,4	35	39	4,4	9,2	3,1	4	3,2	2	1,4	5,5	6,2	11	14	7
B. hybridum	Iran: Susa, SW Iran. USDA:PL239715 (S)	32	41	39	5	8,1	1,6	3	2	1,9	1,5	5	3,9	10	13	8
B. hybridum	Iran: Kohkiloyeh, Gchaemich T.Chogan. MRR:B99-H138 (H)	27,2	36	27	4,7	4,6	1,8	4	2,7	2,1	1,6	12	7,6	9	17	6
B. hybridum	Iran: Kohkiloyeh, Yasooj. MRR:B98-H137 (H)	30,8	51	70	6	6,2	2,8	3	1	3,3	2,7	14	7,2	9,7	18	8
B. hybridum	Iran: Khūzestān, Kalafabad. ABR100* (I)	33,2	41	41	3,1	11	3,3	4	3,2	2,3	1,6	8	8	11	9,6	8
B. hybridum	Iraq: As Sulaymānīyah, Arbet, 30 km S of Arbet. USDA:PL254868 (S)	29,4	37	37	6,4	8,4	3,1	2	1,2	1,8	1,3	5,8	6,6	11	15	7

B. hybridum	Israel: Lehavim. AB&SE:BRA7 (S)	31	38	36	7	4,2	3	4	3	2,3	1,7	8	7,3	9,6	14	9
B. hybridum	Israel: Gilbo'a. AB&SE:BRA26 (S)	26,3	39	35	5	10	3,1	3	1	3,1	1,8	8	5	13	14	7
B. hybridum	Israel: Nahal Bokek. AB&SE:BRA57 (S)	28	34	27	3	3,5	3,1	3	1	2,6	1,9	8	8,2	10	13	8
B. hybridum	Israel: Petah Tikwa. AB&SE:BRA143 (S)	28,7	33	37	5	6,5	2,4	4	3	2,3	1,2	9	7,7	12	13	7
B. hybridum	Israel: Amirim. AB&SE:BRA146 (S)	22,3	40	20	4	8,5	2,8	3	2	2,1	1,3	7	7,6	8,5	13	8
B. hybridum	Israel: Tel Fares. AB&SE:BRA160 (S)	24,6	36	33	5	2,9	1,9	3	3	1,8	1,1	6	8,8	12	16	8
B. hybridum	Israel: Brachyia. AB&SE:BRA221 (S)	27	49	29	6	3	2,4	3	2	2,2	1,6	9	4	11	12	7
B. hybridum	Israel: Sion. AB&SE:BRA293(S)	23,2	44	43	8	3,1	2,2	5	3	2,4	1,8	11	7,5	10	16	7
B. hybridum	Israel: Tel Aviv Univ, Botanical Garden. AB&SE:BRA299 (S)	25,8	34	27	5	2,5	3,9	3	2	2,1	1,4	9	7,2	9,3	7,3	7
B. hybridum	Italy: Sicily, Punta Longa. SH:PLA_1 (S)	28,4	41	37	9,6	8,9	2,5	3	2	1,8	1,2	4	5,1	8,3	9,2	7
B. hybridum	Italy: Sicily, Santa Marina. SH:SMN_1 (S)	30,3	36	24	6,8	9,7	1,9	2	1,3	1,4	0,9	4	4,6	7,6	7,4	6
B. hybridum	Italy: Sicily, Cappella Palatina. SH:VCP_1 (S)	24,6	32	39	9,4	12	2,3	3	2,4	1,7	1,1	5,4	5	7,6	8,6	6
B. hybridum	Leibanon. INRA-V:Aja-1 (S)	33	38	44	7	8,6	2,7	3	2,2	1,8	1,1	7,1	5,9	11	13	7
B. hybridum	Morocco: E Morocco, Oujda, , near Argelia. USDA:PL253334 (S)	34,4	38	37	6,6	12	3,2	4	2,8	2,5	1,8	6,6	6,3	10	12	7
B. hybridum	Pakistan: Khyber Pakhtunkhwa, Pabbi. USDA:PL250647 (S)	33,2	43	43	4,8	10	2,8	3	3	2	1,4	6,4	6	9,6	13	7
B. hybridum	Portugal: Tras-os-Montes,Mogadouro. AM:Mog (S)	31,6	37	40	4	4,5	2,1	4	2	2,6	1,7	10	3	5,3	16	7
B. hybridum	South Africa: E Cape, near Darling. USDA:PL208216 (S)	29,2	40	45	8	11	2,9	3	3,8	1,5	1	5,6	5,2	8,4	8,6	6
B. hybridum	Spain: Alicante, Xávea, playa La Barraca. PC:B101 (S)	32	37	15	6,4	5,4	1,7	3	2,2	1,3	0,8	5,5	6,5	7,6	9,9	7
B. hybridum	Spain: Almeria, Cabo de Gata, Playa de Genoveses. PC:B103 (W)	25	46	51	6	10	2,2	4	3,8	1,8	1,1	7,9	4,7	8,1	11	7
B. hybridum	Spain: Almeria, Cabo de Gata, Playa de Genoveses. PC:B104 (W)	29,2	36	43	4,4	10	2,5	4	3,4	1,9	1,3	7,3	4,8	9,1	10	7
B. hybridum	Spain:Almeria, Cabo de Gata, Playa de Genoveses. PC:B105 (W)	26,6	36	39	4	8,6	2,8	3	2,6	2,3	1,7	7,4	4,7	11	14	7
B. hybridum	Spain: Almeria, Cabo de Gata, Playa de Genoveses. PC:B106 (W)	33,7	38	43	6,3	10	2	4	3,1	2,1	1,5	7,5	4,8	9,1	11	7
B. hybridum	Spain: Almeria, Cabo de Gata, Playa de Genoveses. PC:B107 (W)	29,8	37	41	5,2	9,5	2,3	3	3	1,7	1,1	5,8	4,8	9,3	10	7
B. hybridum	Spain: Barcelona, Montjuich.PC&LM:B37 (W)	30	36	34	3	5,8	2	6	4	2,5	1,5	11	7,5	9	15	6
B. hybridum	Spain: Canarias, Fuerteventura, Puerto del Rosario.INIA-CRF:BGE044244 (S)	29,8	46	44	3	5,9	3,1	6	3	3,2	2,3	13	7,4	11	9,3	8
B. hybridum	Spain: Canarias, Fuerteventura, Betancuria. INIA-CRF:BGE044245 (S)	31	48	39	2,5	4,6	3,2	6	2,5	4	3	13	8,9	12	8,3	8

B. hybridum	Spain: Canarias, Fuerteventura,, Betancuria.INIA-CRF:BGE044246 (S)	33,4	48	47	3	4,8	1,9	6	3	2,9	1,9	11	7,7	11	9,1	5
B. hybridum	Spain: Canarias, Gomera, Vallehermoso, Tamargada. INIA-CRF:BGE044242 (S)	29,2	38	65	4	5,4	2	5	4,5	2,9	1,3	12	6,7	9,2	15	7
B. hybridum	Spain: Canarias, Gomera, Arure_Vallehermoso 3km NE. INIA-CRF:BGE044243 (S)	25	31	48	3	6,1	3,4	4	2	2,3	1,7	12	7,5	8,9	13	8
B. hybridum	Spain: Canarias, Lanzarote, Teguise. INIA-CRF:BGE044247 (S)	30,4	48	48	3	7,5	2	7	3	2,9	2,1	11	8,2	12	9,6	8
B. hybridum	Spain: Canarias, Lanzarote, Teguise.INIA-CRF:BGE044248 (S)	29,2	29	40	3,5	6,5	1,9	5	3,5	2,7	1,7	9,5	8,6	10	18	7
B. hybridum	Spain: Canarias, Tenerife, Buenavista del Norte, Las Canales. INIA-CRF:BGE044238 (S)	29,4	46	40	5,5	12	2,6	5	3,5	2,5	1,7	12	6,8	8,9	17	8
B. hybridum	Spain: Canarias, Tenerife, Buenavista del Norte, Mascas. INIA-CRF:BGE044239 (S)	26,2	44	45	3	7,3	3,6	5	3	2,6	2,1	11	7,5	10	7,6	8
B. hybridum	Spain: Canarias, Tenerife, El Rosario, La esperanza. INIA-CRF:BGE044240 (S)	24,3	43	42	3	6	3,1	4	3,5	2,3	1,7	8	6,8	9,4	12	9
B. hybridum	Spain: Ciudad Real,Puertollano, sierra de Puertollano, Cerro del Castellar. HS:87745-2 (S)	29,2	34	39	8,3	8,9	2	4	2	2,6	2	9,5	8,7	8,7	9,9	7
B. hybridum	Spain: Cordoba, Guadalcazar. INRA:Esp1 (S)	29,2	45	76	5	4,7	2,1	4	2,7	2,9	2,2	13	6,4	8,8	11	7
B. hybridum	Spain: Córdoba, Córdoba.176F** (I)	31,6	43	57	8	10	2,6	4	2,8	1,8	1,4	6,8	8,1	9,9	13	7
B. hybridum	Spain: Girona, Cap de Lladró. PC&LM:B36 (W)	31,5	32	25	4	3,8	1,5	4	3	1,7	1,3	9	8	8	13	6
B. hybridum	Spain: Granada, Sierra Huetor, Puerto de la Mora. PC:B112 (W)	30,6	38	19	7,6	7,2	2,6	3	1,8	2,3	1,6	8	5,7	8,7	11	6
B. hybridum	Spain: Granada, Sierra Huetor, Puerto de la Mora. PC:B130 (W)	29,3	36	12	3	1,7	1,6	2	1,3	1,6	1	5	3,9	8,6	10	7
B. hybridum	Spain: Huelva. 333F** (I)	21,5	40	60	8	6,5	2,5	6	4	2,5	2	10	8,4	10	16	6
B. hybridum	Spain: Huesca, Graus. PC&LM:B16 (W)	31	32	20	3,3	4,4	1,9	4	2,3	2,4	1,2	11	7,8	8,8	16	6
B. hybridum	Spain: Jaen, Sierra Segura, Cortijos Nuevos. PC:B113 (W)	25,2	27	33	5,2	9,1	2,7	4	3,6	2,2	1,6	5,2	6,9	12	14	6
B. hybridum	Spain: Jaen, Sierra Segura, Cortijos Nuevos, Finca La Vaquilla. PC:B114 (W)	30,2	32	45	7,4	7,1	2,6	3	1,4	2,9	2,2	11	6,5	11	15	7
B. hybridum	Spain: Jaén,Sierra Cazorla, Cazorla, Paso del Aire, Mirador de las Palomas. PC:B118 (W)	32	33	44	10,4	9,9	2	3	3	1,7	1,2	5,4	4,2	8	9,9	7
B. hybridum	Spain: Jaén, Hinojares, Hinojares 2. PC:B122 (W)	28,6	32	43	4,4	8,5	2,8	3	2,8	2,4	1,8	6,9	6,7	11	11	7
B. hybridum	Spain: Jaén, Fontanar, Los Cotos2. PC:B124 (W)	27	31	23	4	2,8	1,8	4	3	2,6	2	12	5,7	7,8	14	7
B. hybridum	Spain: Jaén, Fontanar - Los cotos, río Guadiana Menor. PC:B125 (W)	28,2	32	40	3,8	10	2,9	4	3,4	2,4	1,6	5,9	6,4	12	14	8
B. hybridum	Spain: Jaen, Universidad de Jaen. PC:B131 (W)	27,8	36	38	6	5,3	2,3	3	2,4	2	1,4	7,7	5,5	11	14	7

B. hybridum	Spain: Jaén, Sra de Jaen, Salto de la Cabra. PC:B132 (W)	30,4	37	36	8,8	8,1	2,2	3	1,8	2,4	1,8	7,4	5,2	9,2	10	6
B. hybridum	Spain: Jaen, Sra de Jaen, Quiebrajano. PC:B133 (W)	32,8	36	26	8,6	4,4	2,3	3	1,6	2,5	1,8	7,6	5,2	8,7	11	6
B. hybridum	Spain: Jaen, Cazorla, Sierra Quesada, Tiscar, Monasterio de Ntra Sra de Tiscar. PC:B119bis (W)	28,8	39	35	10	8,4	2,8	3	2,6	1,8	1,2	5,5	4,9	8,8	8,3	6
B. hybridum	Spain: Jaen. 137F** (I)	28,6	45	73	9,3	9,3	2,2	7	4,8	2,5	2	12	8,8	10	15	8
B. hybridum	Spain. Málaga, INRA-V:Estepona-0 (S)	25,4	37	37	8	11	3,1	3	2,6	1,9	1,4	5,3	5,3	8,3	9,5	6
B. hybridum	Spain: Málaga, Abdalajis.260F** (I)	28,5	32	73	8	3,2	2,3	4	3	2,5	2	8,5	8,6	8,7	13	7
B. hybridum	Spain: Mallorca, Pto Pollensa. DL&PC:B600 (W)	25,8	34	33	4,5	4,6	2,5	3	2	3	1,7	9	8,2	9	13	7
B. hybridum	Spain: Mallorca, Pto Pollensa, Formentor. DL&PC:B681 (W)	31	41	4,5	1,7	1,2	1	2	1	1,7	0,9	8	7,5	5,1	8,7	6
B. hybridum	Spain: Mallorca, Pto Pollensa, Mal Pas. DL&PC:B701 (W)	30,5	40	12	4	3,7	1,4	3	2	2	1,4	9,7	3,5	3,1	8,3	6
B. hybridum	Spain: Mallorca, Pto Pollensa, St Vicent. DL&PC:B731 (W)	26,4	37	25	8	4,1	1,9	2	1,3	2	1,3	8	4,2	3,6	14	6
B. hybridum	Spain: Mallorca, Pollensa-Soller, Temenia. DL&PC:B741 (W)	27	35	20	4	2,9	1,5	3	2,7	1,9	1,3	9,3	5,5	7,6	13	6
B. hybridum	Spain: Mallorca, Escorca, Tossels Cuvert. DL&PC:B781 (W)	29,4	39	9,7	3	4	1,5	2	1,3	1,6	1,1	7,7	5,7	7,8	12	7
B. hybridum	Spain: Mallorca, Escorca, Pico del Tossel. DL&PC:B791 (W)	30	46	7,6	2,5	1,7	1,3	2	1,3	1,5	1,1	8	5	6,7	9,1	6
B. hybridum	Spain: Mallorca, Escorca, Cuvert. DL&PC:B811 (W)	31,5	45	15	2,5	3,2	1,5	2	1	2,1	1,5	10	6,3	8	11	7
B. hybridum	Spain: Mallorca, Deia. DL&PC:B831 (W)	29	34	14	4,3	3,8	1,8	3	2	2,1	1,4	10	4,9	4,6	10	6
B. hybridum	Spain: Mallorca, Escorca, Sa Calobra. DL&PC:B851 (W)	25	43	20	4	5	1,8	2	2	2,4	1,4	11	3,9	4,2	12	6
B. hybridum	Spain: Mallorca, Paguera, Cala Fornell. DL&PC:B871 (W)	29	36	18	3	3,4	1,3	4	3,3	1,8	1,4	10	6,5	7,9	11	6
B. hybridum	Spain: Mallorca, Valldemosa, Sa Marina. DL&PC:B931 (W)	27,6	39	10	3,4	2,6	1,7	2	1,2	2	1,4	8,6	6,2	7,8	11	5
B. hybridum	Spain: Mallorca, Llucmajor, Algaida. DL&PC:B1101 (W)	28,8	41	35	3,7	2,6	1,6	5	3	3,5	2,5	16	6,9	9,2	9	7
B. hybridum	Spain: Menorca, Foruell, Torre de Foruell. DL&PC:B1001 (W)	28	37	20	4,7	3	1,3	3	2,3	1,7	1,1	9,3	4,5	6,4	9,7	6
B. hybridum	Spain: Menorca, Ciutadella, Port. DL&PC:B1011 (W)	28,1	36	29	4	6,3	2,1	4	2,8	2,2	1,6	9,8	6,2	8,8	14	7
B. hybridum	Spain: Murcia,Espuña. AM:Espuña (S)	34,8	43	49	6,5	2,8	0,8	4	2,7	2,5	1,6	9	4,3	8,1	16	8
B. hybridum	Spain: Murcia, Alhama de Murcia, Srra Espuña1. PC:B137 (W)	28,4	41	34	4,6	11	2,3	4	3	2,1	1,4	8,8	5,8	11	12	7
B. hybridum	Spain: Murcia, Alhama de Murcia, Srra Espuña2. PC:B138 (W)	33	38	71	7,4	11	3,1	4	3,8	2,2	1,5	7,6	5,2	8,1	12	7
B. hybridum	Spain: Murcia, Alhama de Murcia, Srra Espuña3. PC:B139 (W)	29,4	41	43	5,4	9,5	2,2	3	2,6	2	1,3	8,3	5,5	9,9	9,9	7
B. hybridum	Spain: Tarragona, Amposta. PC&LM:B39 (W)	29,3	39	24	3,3	3,4	1,6	4	3,3	1,8	1,4	8,3	7,3	7,3	14	6
B. hybridum	Spain: Tarragona, Poble Nou del Delta. PC&LM:B40 (W)	32,6	38	18	2	2,9	2	5	2,8	2,8	1,5	10	8,8	9,6	14	7

B. hybridum	Spain: Teruel, Calaceite. PC&LM:B41 (W)	26,2	32	18	2	2,1	1,7	4	2,4	2,3	1,1	9,2	5,6	7	7,6	6
B. hybridum	Spain: Zaragoza, Belchite. PC&LM:B42 (W)	31,7	39	12	2,3	2,1	1,6	3	2,3	1,8	1,1	10	5,3	7,3	8,3	6
B. hybridum	Uruguay. USDA:PL372187 (S)	27	36	42	7	11	3,6	4	4	2	1,4	6,8	4,3	8,4	10	6

Table S2. Morphological variables used in the phenotypic analysis. Results of the Kolmogorov-Smirnov normality test. Significance: ***: p<0.001; **: p<0.01; *: p<0.5; n. s.: non-significant.

Trait	Code	Statistic
Leaf guard cell length in the stomata (mm)	LGCL	0.076*
Pollen grain length (mm)	PGL	0.074*
Plant height (cm)	H	0.074*
Number of nodes of tallest culm	NNTC	0.113***
Second leaf length from the base of the plant (cm)	SLL	0.107***
Second leaf width (mm)	SLW	0.081**
Inflorescence length (cm)	IL	0.082**
Number of spikelets per inflorescence	NSI	0.099***
Spikelet total length, without awns (cm)	SLA	0.094***
Spikelet length from the base to the apex of the fourth lemma, without awns (cm)	SLB	0.095***
Number of flowers per inflorescence	NFS	$0.064^{n.s.}$
Upper glume length (mm)	UGL	$0.060^{n.s.}$
Lemma length from the basal floret (mm)	LL	$0.050^{n.s.}$
Awn length, the longest within the spikelet (mm)	AL	0.080*
Caryopsis length (mm)	CL	$0.032^{n.s.}$

Table S3. Pairwise Spearman correlation coefficients between phenotypic traits (averaged values) analyzed in wild individuals of *B. distachyon*, *B. stacei* and *B. hybridum*. Significant correlation values (p<0.001) are highlighted in bold.

	LGCL	PGL	H	NNTC	SLL	SLW	IL	NSI	SLA	SLB	NFI	UGL	LL	AL	CL
LGCL															
PGL	**0.54**														
H	0.14	0.21													
NNTC	0.11	0.16	**0.52**												
SLL	0.33	0.26	**0.66**	**0.56**											
SLW	0.16	0.16	**0.53**	0.33	**0.69**										
IL	0.15	0.20	**0.70**	0.09	0.37	0.40									
NSI	0.03	0.01	**0.65**	0.18	0.46	0.38	**0.75**								
SLA	0.25	0.38	0.41	-0.02	0.18	0.34	**0.65**	0.20							
SLB	0.19	0.37	0.39	0.03	0.15	0.29	0.58	0.16	**0.89**						
NFI	0.01	0.22	0.04	-0.38	-0.31	-0.13	0.40	0.07	**0.62**	**0.59**					
UGL	-0.11	-0.04	0.07	-0.19	-0.15	0.10	0.29	0.15	0.30	0.32	0.35				
LL	0.24	0.24	0.49	0.14	0.45	0.57	0.55	0.28	**0.59**	**0.56**	0.07	0.32			
AL	-0.03	0.04	0.23	0.06	0.08	0.19	0.40	0.21	0.40	0.39	0.24	0.34	0.42		
CL	0.37	0.44	0.50	0.17	0.40	0.41	0.52	0.24	0.58	0.55	0.12	0.12	0.64	0.38	

Table S4. Loadings of phenotypic traits onto the first PCA components. Highest contributions of characters to each component are highlighted in bold.

Phenotypic trait	C 1	C 2	C 3
LGCL	0.043	0.451	**-0.608**
PGL	0.092	**0.876**	0.301
H	**0.982**	-0.112	0.042
NNTC	0.061	-0.004	-0.217
SLL	0.114	0.054	-0.465
SLW	0.019	0.004	-0.037
IL	0.053	0.002	0.091
NSS	0.034	-0.020	-0.002
SLA	0.013	0.028	0.050
SLB	0.010	0.022	0.049
NFI	0.014	0.091	0.421
UGL	0.010	-0.010	0.147
LL	0.046	0.030	0.006
AL	0.041	-0.001	0.246
CL	0.028	0.055	0.010

Table S5. Contribution of phenotypic variables to the first canonical discriminant functions obtained for the two data sets of individuals of *B. distachyon*. *B. stacei* and *B. hybridum* analyzed: W (174 wild populations data set). I + W (6 inbred lines + 174 wild populations data set). Variables that contributed more to the functions are highlighted in bold.

	W			**I+W**	
	1	2		1	2
LGCL	**0.545***	0.391	**LGCL**	**0.564***	0.375
CL	**0.475***	-0.066	**CL**	**0.458***	-0.051
PGL	**0.424***	0.249	**PGL**	**0.442***	0.243
SLL	0.347*	0.019	**SLA**	0.351*	-0.053
SLA	0.344*	-0.041	**SLL**	0.339*	0.006
LL	0.298*	-0.152	**LL**	0.303*	-0.143
H	0.293*	-0.139	**H**	0.298*	-0.14
SLB	0.272*	-0.097	**SLB**	0.276*	-0.101
SLW	0.257*	-0.153	**SLW**	0.238*	-0.174
NNTC	0.125*	0.117	**NNTC**	0.129*	0.119
IL	0.396	**-0.519***	**IL**	0.391	**-0.528***
NSI	0.177	-0.188*	**NSI**	0.17	-0.178*
AL	0.135	-0.163*	**AL**	0.128	-0.143*
UGL	-0.001	0.058*	**UGL**	-0.003	0.069*
NFI	0.055	-0.057*	**NFI**	0.06	-0.064*

Table S6. Contribution of phenotypic variables to the first canonical discriminant functions obtained for individuals from 41 wild populations of *B. distachyon*. Variables that contribute more to the functions are highlighted in bold.

	Function	
	1	2
H	0.**565(*)**	0.191
LGCL	-0.108(*)	-0.063
UGL	0.002	0.**656**(*)
AL	-0.048	0.**464**(*)
NNTC	0.317	-0.**461**(*)
NSS	0.154	0.411(*)
PGL	0.022	0.258(*)
LL	0.022	0.158(*)
CL	0.057	-0.026
SLB	0.045	0.262
SLW	0.049	0.140
SLL	0.286	-0.022
IL	0.109	0.451
NFI	-0.064	0.384
SLA	-0.047	0.221

Table S7. Contribution of phenotypic variables to the first canonical discriminant functions obtained for individuals from 29 wild populations of *B. stacei*. Variables that contribute more to the functions are highlighted in bold.

	Function						
	1	2	3	4	5	6	7
IL	**-0.111(*)**	0.019	0.076	-0.052	0.075	0.071	0.034
SLB	0.027	**0.185(*)**	-0.093	0.025	-0.032	0.069	0.046
SLA	0.015	**0.167(*)**	-0.107	-0.133	0.051	0.096	0.011
NNTC	-0.083	0.021	**0.328(*)**	0.229	0.020	0.060	0.098
AL	-0.008	0.095	**0.266(*)**	0.095	-0.034	0.142	0.241
UGL	-0.014	-0.018	0.135	**0.268(*)**	-0.081	-0.085	-0.111
H	-0.217	-0.030	0.130	-0.123	**0.493(*)**	0.228	0.143
NSS	-0.092	-0.070	0.131	-0.089	**0.239(*)**	-0.138	-0.030
SLL	-0.097	-0.102	0.122	-0.155	0.085	**0.630(*)**	-0.123
CL	0.020	0.142	-0.005	0.291	0.229	**0.305(*)**	-0.005
PGL	0.129	0.200	0.023	0.233	0.128	**0.303(*)**	0.294
LGCL	0.054	0.083	-0.137	0.008	-0.100	**-0.180(*)**	0.108
SLW	-0.028	0.011	0.121	-0.156	0.060	0.234	**-0.530(*)**
NFI	0.055	0.094	-0.130	-0.073	0.042	0.027	**0.267(*)**
LL	-0.022	0.104	0.190	-0.208	0.205	-0.017	**-0.209(*)**

Table S8. Contribution of phenotypic variables to the first canonical discriminant functions obtained for individuals from 89 wild populations of *B. hybridum*. Variables that contribute more to the functions are highlighted in bold.

	Function				
	1	2	3	4	5
H	0.**508**(*)	-0.219	-0.431	0.009	0.074
SLW	0.**440**(*)	-0.053	0.065	0.053	0.094
CL	0.**402**(*)	0.120	0.174	0.136	0.142
NNTC	0.172	-0.**571**(*)	-0.026	0.006	0.232
UGL	0.141	0.**486**(*)	0.038	-0.203	-0.136
NFI	-0.086	0.**420**(*)	-0.195	0.152	-0.245
SLL	0.337	-0.388(*)	-0.201	-0.043	0.020
IL	0.291	0.279	**-0.444(*)**	-0.275	-0.415
NSS	0.168	-0.069	**-0.394(*)**	-0.342	0.010
AL	0.114	0.134	**0.343(*)**	-0.158	0.112
PGL	0.129	0.252	-0.199	**0.527(*)**	-0.033
LGCL	0.008	-0.085	-0.133	**-0.286(*)**	0.071
SLB	0.159	0.190	-0.065	0.342	**-0.590(*)**
LL	0.504	0.094	0.390	-0.138	**-0.530(*)**
SLA	0.145	0.278	-0.118	0.174	**-0.500(*)**

Table S9. Annotation of 434 'explanatory' nominal mass fingerprint signals by targeted accurate *m/z* data analysis and MZedDB database search at MSI level of identification 2. The *m/z* signal with duplicate annotations, i.e., other adducts or isotopes of same metabolite, are indicated as plain (un-bold) text .

PW Class	Nominal *m/z*	Ionisation Mode	Accurate *m/z*	Max. Intensity	Theoretical *m/z*	Molecular Formula	Putative Ionization Product	Adduct	PPM Error
2N=10~2N=30	**71.09**	**Negative**	**71.01350**	**88389**	**71.01385**	**C3H4O2**	**Propenoate**	**[M-H]1-**	**-4.97**
E137F00h~E484F00h	**72.09**	**Negative**	72.00872	723	72.00910	C2H3NO2	Imino glycine	[M-H]1-	-5.36
			72.01682	**1230**	**-**	**-**	**Unknown**	**-**	**-**
E160F00h~E485F00h	**73.09**	**Negative**	**72.99276**	**17632**	**72.99312**	**C2H2O3**	**Glyoxylate**	**[M-H]1-**	**-4.86**
			73.02914	**2623**	**73.02950**	**C3H6O2**	**Propanoate**	**[M-H]1-**	**-5.00**
2N=10~2N=30	**87.09**	**Negative**	**87.00848**	**97834**	**87.00877**	**C3H4O3**	**Pyruvate**	**[M-H]1-**	**-3.26**
E115F00h~E176F00h	**88.09**	**Negative**	**88.04009**	**32696**	**88.04040**	**C3H7NO2**	**Sarcosine**	**[M-H]1-**	**-3.52**
E129F00h~E137F00h	**89.09**	**Negative**	**88.98781**	**29000**	**88.98803**	**C2H2O4**	**Oxalate**	**[M-H]1-**	**-2.56**
			89.02416	**83599**	**89.02442**	**C3H6O3**	**Lactate**	**[M-H]1-**	**-2.90**
2N=10~2N=20	91.09	Negative	90.99288	2589	90.99312	C7H4O6	Chelidonate	[M-2H]2-	-2.60
E137F00h~E160F00h	**100**	**Negative**	**100.04012**	**741**	**100.04040**	**C4H7NO2**	**Homoserine Lactone**	**[M-H]1-**	**-2.82**
			100.07653	483	100.07679	C5H11NO	5-Amino pentanal	[M-H]1-	-2.57
E137F00h~E485F00h	**101.09**	**Negative**	**101.00599**	**1569**	**-**	**-**	**Unknown**	**-**	**-**
			101.02414	**13018**	**101.02442**	**C4H6O3**	**Oxo butanoate**	**[M-H]1-**	**-2.75**
E115F00h~E260F00h	**102.09**	**Negative**	**102.05576**	**34229**	**102.05605**	**C4H9NO2**	**γ-Amino butyrate**	**[M-H]1-**	**-2.86**
2N=10~2N=30	**103.09**	**Negative**	**103.00346**	**5226**	**103.00368**	**C3H4O4**	**Hydroxy pyruvate**	**[M-H]1-**	**-2.16**
			103.03980	**1511**	**103.04007**	**C4H8O3**	**Hydroxy butyrate**	**[M-H]1-**	**-2.60**
E114F00h~E115F00h	104.09	Negative	104.03508	18939	104.03532	C3H7NO3	Serine	[M-H]1-	-2.28
2N=10~2N=20	**105.09**	**Negative**	**105.01908**	**34360**	**105.01933**	**C3H6O4**	**Glycerate**	**[M-H]1-**	**-2.41**
E114F00h~E480F00h	**107.09**	**Negative**	**107.05008**	**502**	**107.05024**	**C7H8O**	***p*-Cresol**	**[M-H]1-**	**-1.48**
E114F00h~E176F00h	116.09	Negative	**116.00687**	**4668**	**-**	**-**	**Unknown**	**-**	**-**
			116.07155	1962	116.07170	C5H11NO2	Valine	[M-H]1-	-1.31
E137F00h~E333F00h	**117**	**Negative**	**117.01909**	**11733**	**117.01933**	**C4H6O4**	**Succinate**	**[M-H]1-**	**-2.08**
2N=20~2N=30	118.09	Negative	118.05079	19614	118.05097	C4H9NO3	Threonine	[M-H]1-	-1.50
E137F00h~E485F00h	**119**	**Negative**	**118.93055**	**1684**	**118.93059**	**H3O3P**	**Phosphonate**	**[M+K-2H]1-**	**-0.32**
			118.94190	5134	118.94205	H2O4S	Sulfate	[M+Na-2H]1-	-1.28

			119.03482	**1284**	**119.03498**	**C4H8O4**	**Erythrose / Threose**	**[M-H]1-**	**-1.37**
			119.05007	**3481**	**119.05024**	**C8H8O**	**4-Hydroxy styrene**	**[M-H]1-**	**-1.41**
2N=10~2N=20	**121**	**Negative**	120.99634	797	120.99649	C3H6O3S	3-Mercapto lactate	[M-H]1-	-1.26
			121.02928	**2939**	**121.02950**	**C7H6O2**	**Benzoate**	**[M-H]1-**	**-1.84**
			121.06566	**716**	**121.06589**	**C8H10O**	**2,4-Dimethyl phenol**	**[M-H]1-**	**-1.88**
E115F00h~E162F00h	**123**	**Negative**	**123.00857**	**737**	**123.00877**	**C6H4O3**	**2-Hydroxy-1,4-Benzoquinone**	**[M-H]1-**	**-1.61**
			123.04494	**524**	**123.04515**	**C7H8O2**	**3-Hydroxybenzyl alcohol**	**[M-H]1-**	**-1.73**
E114F00h~E137F00h	**124**	**Negative**	**124.00726**	**428**	**124.00739**	**C2H7NO3S**	**Taurine**	**[M-H]1-**	**-1.06**
			124.01654	**846**	**124.01691**	**C2H8NO3P**	**2-Aminoethyl phosphonate**	**[M-H]1-**	**-2.94**
			124.04027	**513**	**124.04040**	**C6H7NO2**	**3,6-Dihydro nicotinate**	**[M-H]1-**	**-1.06**
			124.05179	**430**	**124.05164**	**C5H7N3O**	**5-Methyl cytosine**	**[M-H]1-**	**1.25**
E129F00h~E137F00h	**125**	**Negative**	**125.02426**	**1306**	**125.02442**	**C6H6O3**	**Pyrogallol**	**[M-H]1-**	**-1.26**
			125.06060	**569**	**125.06080**	**C7H10O2**	**3-Heptynoate**	**[M-H]1-**	**-1.62**
E115F00h~E176F00h	**126**	**Negative**	**126.01957**	**545**	**126.01967**	**C5H5NO3**	**2,3,6-Trihydroxy pyridine**	**[M-H]1-**	**-0.77**
2N=10~2N=20	**129.09**	**Negative**	**128.95931**	**2905**	**-**	**-**	**Unknown**	**-**	**-**
			129.01918	**28289**	**129.01933**	**C5H6O4**	**Glutaconate**	**[M-H]1-**	**-1.19**
			129.03854	**1499**	**-**	**-**	**Unknown**	**-**	**-**
			129.05555	**1086**	**129.05572**	**C6H10O3**	**5-Oxo hexanoate**	**[M-H]1-**	**-1.30**
E137F00h~E160F00h	**132.09**	**Negative**	**132.03001**	**133167**	**132.03023**	**C4H7NO4**	**Aspartate**	**[M-H]1-**	**-1.68**
2N=10~2N=30	**133.09**	**Negative**	**133.01404**	**689515**	**133.01425**	**C4H6O5**	**Malate**	**[M-H]1-**	**-1.56**
2N=10~2N=30	134.09	Negative	134.01745	26979	-	-	13C Isotope of Malate	[M-H]1-	-
			134.04706	1023	134.04722	C5H5N5	Adenine	[M-H]1-	-1.18
2N=10~2N=30	**135**	**Negative**	**134.91583**	**11326**	**134.91599**	**H2O4S**	**Sulfate**	**[M+K-2H]1-**	**-1.18**
			135.02970	**55697**	**135.02990**	**C4H8O5**	**Threonate**	**[M-H]1-**	**-1.47**
2N=10~2N=20	**136**	**Negative**	**135.92070**	**23574**	**-**	**-**	**Unknown**	**-**	**-**
			136.01640	**1971**	**-**	**-**	**Unknown**	**-**	**-**
			136.03305	**1436**	**-**	**-**	**Unknown**	**-**	**-**
			136.04023	**694**	**136.04040**	**C7H7NO2**	***p*-Amino benzoate**	**[M-H]1-**	**-1.26**
			136.07649	631	136.07679	C8H11NO	Tyramine	[M-H]1-	-2.18
E129F00h~E137F00h	**138**	**Negative**	137.99568	2854	137.99628	C4H7NO2	Aceto acetamide	[M+K-2H]1-	-4.38
			138.01932	**463**	**138.01967**	**C6H5NO3**	**6-Hydroxy nicotinate**	**[M-H]1-**	**-2.51**
			138.05577	**1700**	**138.05605**	**C7H9NO2**	**Trigonelline**	**[M-H]1-**	**-2.04**
2N=10~2N=20	**139**	**Negative**	**138.97999**	**1178**	**138.98019**	**C2H5O5P**	**Acetyl Phosphate**	**[M-H]1-**	**-1.41**

			139.00351	**29424**	**139.00368**	**C3H2O2**	**Propynoate**	**[2M-H]1-**	**-1.24**
			139.03986	**712**	**139.04007**	**C7H8O3**	**4-Hydroxy methyl catechol**	**[M-H]1-**	**-1.50**
			139.07618	**668**	**139.07645**	**C8H12O2**	**2-Octynoate**	**[M-H]1-**	**-1.96**
2N=10~2N=30	**142**	**Negative**	**142.05078**	**826**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=20	**143.09**	**Negative**	142.97488	1195	142.97522	C3H6O4	Glycerate	[M+K-2H]1-	-2.34
			142.99836	**18394**	**-**	**-**	**Unknown**	**-**	**-**
			143.03478	**1303**	**143.03498**	**C6H8O4**	**3-Methyl glutaconate**	**[M-H]1-**	**1.21**
			143.07116	**956**	**143.07137**	**C7H12O3**	**n-Valeryl acetate**	**[M-H]1-**	**2.71**
			143.10763	**816**	**143.10775**	**C8H16O2**	**Caprylate**	**[M-H]1-**	**-0.86**
E114F00h~E137F00h	**144.09**	**Negative**	**144.03006**	**577**	**144.03023**	**C5H7NO4**	**2-Oxo glutaramate**	**[M-H]1-**	**-1.19**
			144.06638	**751**	**144.06662**	**C6H11NO3**	**5-Hydroxy-pipecolate**	**[M-H]1-**	**-1.65**
E137F00h~E160F00h	**145.09**	**Negative**	**145.01397**	**5041**	**145.01425**	**C5H6O5**	**Oxoglutarate**	**[M-H]1-**	**-1.92**
			145.05044	**678**	**145.05063**	**C6H10O4**	**Adipate**	**[M-H]1-**	**-1.33**
			145.06165	**41934**	**145.06187**	**C5H10N2O3**	**Alanyl glycine**	**[M-H]1-**	**-1.49**
2N=10~2N=30	**146.09**	**Negative**	**145.94952**	**9574**	**-**	**-**	**Unknown**	**-**	**-**
			146.04567	**223467**	**146.04588**	**C5H9NO4**	**3-Methyl aspartate**	**[M-H]1-**	**-1.45**
2N=20~2N=30	**147**	**Negative**	**147.02966**	**10402**	**147.02990**	**C5H8O5**	**Hydroxy glutarate**	**[M-H]1-**	**1.07**
			147.04507	**511**	**147.04515**	**C9H8O2**	**Cinnamate**	**[M-H]1-**	**-0.56**
			147.04901	6893	-	-	13C Isotope of 3-Methyl aspartate	[M-H]1-	-
			147.06601	**1087**	**147.06628**	**C6H12O4**	**Mevalonate**	**[M-H]1-**	**-1.86**
Pilar analysis	**148.09**	**Negative**	148.04368	587	148.04378	C5H11NO2S	L-Methionine	[M-H]1-	-0.65
			148.04985	**1064**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=20	**151**	**Negative**	**151.03991**	**2748**	**151.04007**	**C8H8O3**	**Methyl salicylate / Vanillin**	**[M-H]1-**	**-1.05**
2N=20~2N=30	**152.09**	**Negative**	**151.98280**	**2216**	**-**	**-**	**Unknown**	**-**	**-**
			152.01135	607	152.01193	C5H9NO2	Proline	[M+K-2H]1-	-3.84
			152.03502	**547**	**152.03532**	**C7H7NO3**	***p*-Amino salicylate**	**[M-H]1-**	**-1.95**
			152.04815	736	152.04838	C5H11NO2	Valine	[M+Cl]1-	-1.51
			152.07148	**394**	**152.07170**	**C8H11NO2**	**Dopamine**	**[M-H]1-**	**-1.46**
E333F00h~E484F00h	**157**	**Negative**	**156.96285**	**1709**	**-**	**-**	**Unknown**	**-**	**-**
			157.03637	**1052**	**157.03671**	**C4H6N4O3**	**Allantoin**	**[M-H]1-**	**-2.19**
			157.05032	712	157.05063	C7H10O4	2-Isopropyl maleate	[M-H]1-	-1.99
			157.08683	**709**	**157.08702**	**C8H14O3**	**2-Keto-N-caprylate**	**[M-H]1-**	**-1.20**
E137F00h~E480F00h	**158**	**Negative**	158.04566	636	158.04588	C6H9NO4	N-Methyl-2-oxoglutaramate	[M-H]1-	-1.40

			158.08205	**512**	**158.08227**	**C7H13NO3**	**Valeryl glycine**	**[M-H]1-**	**-1.37**
2N=10~2N=20	**163**	**Negative**	**162.93962**	**340840**	**-**	**-**	**Unknown**	**-**	**-**
			163.03983	**29190**	**163.04007**	**C9H8O3**	***p*-Coumarate**	**[M-H]1-**	**-1.46**
2N=20~2N=30	**165**	**Negative**	**164.93770**	**18934**	**-**	**-**	**Unknown**	**-**	**-**
			165.01912	**2020**	**165.01933**	**C8H6O4**	**Phthalate**	**[M-H]1-**	**-1.29**
			165.04032	**18130**	**165.04046**	**C5H10O6**	**Xylonate**	**[M-H]1-**	**-0.87**
			165.05537	**609**	**165.05572**	**C9H10O3**	**Caffeyl alcohol**	**[M-H]1-**	**-2.11**
2N=10~2N=20	**168**	**Negative**	168.02756	436	168.02783	C5H9NO4	Glutamate	[M+Na-2H]1-	-1.59
			168.04292	**862**	**168.04323**	**C6H13NO2**	**Leucine / Isoleucine**	**[M+K-2H]1-**	**-1.87**
E114F00h~E160F00h	**171**	**Negative**	170.96990	784	170.97013	C4H6O5	Malate	[M+K-2H]1-	-1.35
			171.00625	**1079**	**171.00640**	**C3H9O6P**	**Glycerol 3-phosphate**	**[M-H]1-**	**-0.88**
			171.02979	**1336**	**171.02990**	**C7H8O5**	**3-Dehydro shikimate**	**[M-H]1-**	**-0.63**
2N=10~2N=30	**173.09**	**Negative**	**173.00904**	**29910**	**173.00916**	**C6H6O6**	**Dehydro ascorbate**	**[M-H]1-**	**-0.71**
			173.04536	**10551**	**173.04555**	**C7H10O5**	**Shikimate**	**[M-H]1-**	**-1.09**
			173.08170	**1955**	**173.08193**	**C8H14O4**	**Ethyl adipate**	**[M-H]1-**	**-1.35**
2N=10~2N=30	174.09	Negative	174.04055	774	174.04080	C6H9NO5	N-Acetyl aspartate	[M-H]1-	-1.42
			174.04871	815	-	-	13C Isotope of Shikimate	[M-H]1-	-
2N=10~2N=30	**179.09**	**Negative**	**179.03491**	**2291**	**179.03498**	**C9H8O4**	**Caffeate**	**[M-H]1-**	**-0.41**
			179.05589	2268	179.05611	C6H12O6	Glucose	[M-H]1-	-1.25
			179.07106	**457**	**179.07137**	**C10H12O3**	**Coniferyl Alcohol**	**[M-H]1-**	**-1.72**
2N=10~2N=20	**181.09**	**Negative**	**181.01389**	**844**	**181.01425**	**C8H6O5**	**4-Hydroxy phthalate**	**[M-H]1-**	**-1.98**
			181.05044	**755**	**181.05063**	**C9H10O4**	**Dihydro caffeate**	**[M-H]1-**	**-1.07**
E115F00h~E160F00h	**182.09**	**Negative**	**181.93438**	**1582**	**-**	**-**	**Unknown**	**-**	**-**
			181.94686	**1114**	**-**	**-**	**Unknown**	**-**	**-**
			182.04557	**1495**	**182.04588**	**C8H9NO4**	**5-Methoxy-3-hydroxyanthranilate**	**[M-H]1-**	**-1.71**
2N=10~2N=30	**183.09**	**Negative**	**182.99338**	**9133**	**182.99351**	**C7H4O6**	**Chelidonate**	**[M-H]1-**	**-0.73**
			183.02984	**760**	**183.02990**	**C8H8O5**	**3-O-Methyl gallate**	**[M-H]1-**	**-0.32**
			183.10245	**879**	**183.10267**	**C10H16O3**	**5-Oxo-7E-decenoate**	**[M-H]1-**	**-1.19**
E114F00h~E137F00h	**184.09**	**Negative**	**183.99615**	**1148**	**-**	**-**	**Unknown**	**-**	**-**
			184.00154	**828**	**184.00165**	**C3H8NO6P**	**O-Phospho serine**	**[M-H]1-**	**-0.60**
E114F00h~E480F00h	**185.09**	**Negative**	**184.98556**	**21029**	**184.98567**	**C3H7O7P**	**3-Phospho glycerate**	**[M-H]1-**	**-0.57**
			185.02198	657	185.02201	C9H8O3	*p*-Coumarate	[M+Na-2H]1-	-0.18
2N=20~2N=30	**187.09**	**Negative**	**187.09734**	**880**	**187.09758**	**C9H16O4**	**Azelaic acid**	**[M-H]1-**	**-1.30**

2N=10~2N=30	**191.09**	**Negative**	**191.01952**	**493719**	**191.01973**	**C6H8O7**	**Citrate**	**[M-H]1-**	**-1.09**
			191.05585	**164745**	**191.05611**	**C7H12O6**	**Quinate**	**[M-H]1-**	**-1.38**
2N=10~2N=30	192.09	Negative	192.02302	20039	-	-	13C Isotope of Citrate	[M-H]1-	-
			192.05922	6070	-	-	13C Isotope of Quinate	[M-H]1-	-
E137F00h~E480F00h	**193.09**	**Negative**	**193.05061**	**13417**	**193.05063**	**C10H10O4**	**Ferulate**	**[M-H]1-**	**-0.12**
2N=10~2N=30	**194.09**	**Negative**	**194.04572**	**556**	**194.04588**	**C9H9NO4**	**Salicyl urate**	**[M-H]1-**	**-0.83**
			194.05389	**1033**	**194.05471**	**C6H11N3O3**	**2-Oxo arginine**	**[M+Na-2H]1-**	**-4.23**
2N=10~2N=20	**195.18**	**Negative**	194.92756	669	194.92749	H2O4S	Sulfate	[2M-H]1-	0.35
			194.94634	**3658**	**194.94652**	**H3O4P**	**Phosphorate**	**[2M-H]1-**	**-0.92**
			195.05084	56939	195.05103	C6H12O7	Gluconate	[M-H]1-	-0.96
E176F00h~E480F00h	**197.18**	**Negative**	**197.00909**	**915**	**197.00916**	**C8H6O6**	**3,4-Dihydroxy phthalate**	**[M-H]1-**	**-0.37**
			197.02210	**511**	**197.02217**	**C7H12O4**	**Pimelate**	**[M+K-2H]1-**	**-0.33**
			197.04528	**784**	**197.04555**	**C9H10O5**	**Syringate**	**[M-H]1-**	**-1.36**
E114F00h~E115F00h	**198**	**Negative**	198.01718	1795	198.01730	C4H10NO6P	*o*-Phospho homoserine	[M-H]1-	-0.61
			198.04023	**1046**	**198.04080**	**C8H9NO5**	**Clavulanate**	**[M-H]1-**	**-2.86**
2N=20~2N=30	**199.09**	**Negative**	**198.91787**	**577**	**198.91790**	**H4O7P2**	**Pyrophosphate**	**[M+Na-2H]1-**	**-0.15**
			199.00123	**975**	**199.00132**	**C4H9O7P**	**Erythrose-4-phosphate**	**[M-H]1-**	**-0.43**
			199.13390	**737**	**199.13397**	**C11H20O3**	**8-Propionyl caprylate**	**[M-H]1-**	**-0.34**
2N=10~2N=20	**201.09**	**Negative**	**201.00398**	**544**	**201.00408**	**C7H6O7**	**4-Oxalo mesaconate**	**[M-H]1-**	**-0.49**
			201.04026	**483**	**201.04046**	**C8H10O6**	**cis-(Homo)$_2$aconitate**	**[M-H]1-**	**-1.01**
			201.11298	603	201.11323	C10H18O4	Sebacate	[M-H]1-	-1.26
2N=10~2N=20	**203.09**	**Negative**	**203.01972**	**55332**	**203.01973**	**C7H8O7**	**Oxaloglutarate**	**[M-H]1-**	**-0.04**
2N=20~2N=30	**204.09**	**Negative**	204.02305	2530	-	-	13C Isotope of oxaloglutarate	[M-H]1-	-
			204.05154	**774**	**204.05224**	**C8H15NOS2**	**Lipoamide**	**[M-H]1-**	**-3.41**
2N=10~2N=20	**207.09**	**Negative**	**206.94689**	**702**	**206.94663**	**C3H7O6P**	**Dihydroxyacetone phosphate**	**[M+K-2H]1-**	**1.24**
			206.96775	616	206.96761	C3H7O7P	3-Phospho glycerate	[M+Na-2H]1-	0.67
			207.06622	**912**	**207.06628**	**C11H12O4**	**Sinapaldehyde**	**[M-H]1-**	**-0.30**
2N=10~2N=20	**208.18**	**Negative**	**208.06149**	**752**	**208.06153**	**C10H11NO4**	**4-Hydroxyphenyl acetyl glycine**	**[M-H]1-**	**-0.20**
E114F00h~E137F00h	**210.09**	**Negative**	**209.94877**	**10220**	**-**	**-**	**Unknown**	**-**	**-**
			210.04068	**847**	**210.04080**	**C9H9NO5**	**DIMBOA**	**[M-H]1-**	**-0.56**
E114F00h~E137F00h	**211.09**	**Negative**	211.00114	912	211.00143	C7H10O5	Shikimate	[M+K-2H]1-	-1.37
			211.02474	**941**	**211.02481**	**C9H8O6**	**3-(2-Carboxyethenyl)-cis,cis-muconate**	**[M-H]1-**	**-0.35**
			211.03746	544	211.03788	C7H12O5	2-Isopropyl malate	[M+Cl]1-	-1.97

E114F00h~E137F00h	**212.09**	**Negative**	**211.99572**	**485**	**211.99657**	**C4H8NO7P**	**4-Phospho aspartate**	**[M-H]1-**	**-3.99**
			212.05646	**464**	**212.05645**	**C9H11NO5**	**N,N-Dihydroxy tyrosine**	**[M-H]1-**	**0.06**
E137F00h~E162F00h	**213.09**	**Negative**	**213.01704**	**859**	**213.01697**	**C5H11O7P**	**Deoxyribose 5-phosphate**	**[M-H]1-**	**0.35**
			213.04049	**812**	**213.04046**	**C9H10O6**	**2-Hydroxy-6-oxonona-2,4-diene-1,9-dioate**	**[M-H]1-**	**0.13**
			213.14955	**566**	**213.14962**	**C12H22O3**	**4-Keto laurate**	**[M-H]1-**	**-0.32**
E114F00h~E115F00h	215.09	Negative	215.03268	1358	215.03279	C6H12O6	Glucose	[M+Cl]1-	-0.52
E114F00h~E115F00h	**216.09**	**Negative**	**216.02783**	**1081**	**216.02798**	**C6H13NO5**	**Glucosamine**	**[M+K-2H]1-**	**-0.69**
E115F00h~E129F00h	217.18	Negative	217.02960	848	-	-	37Cl Isotope of Glucose	[M+Cl]1-	-
E115F00h~E485F00h	**218.09**	**Negative**	**217.97904**	**1438**	-	-	**Unknown**	-	-
			218.10321	603	218.10340	C9H17NO5	Pantothenate	[M-H]1-	-0.86
2N=10~2N=30	220.09	Negative	219.97840	848	219.97833	C3H8NO6P	*O*-Phospho serine	[M+Cl]1-	0.33
2N=10~2N=20	**221.09**	**Negative**	220.94935	5273	220.94940	C7H4O6	Chelidonate	[M+K-2H]1-	-0.20
			221.06666	**684**	**221.06668**	**C8H14O7**	**6-Acetyl glucose**	**[M-H]1-**	**-0.08**
E137F00h~E485F00h	**222.09**	**Negative**	221.97526	502	-	-	37Cl Isotope of O-Phospho serine	[M+Cl]1-	-
			222.07707	**653**	**222.07718**	**C11H13NO4**	**N-Acetyl tyrosine**	**[M-H]1-**	**-0.50**
E114F00h~E137F00h	**223.09**	**Negative**	222.94148	1693	222.94155	C3H7O7P	3-Phospho glycerate	[M+K-2H]1-	-0.31
			223.06103	**646**	**223.06120**	**C11H12O5**	**Sinapate**	**[M-H]1-**	**-0.75**
			223.13403	688	223.13397	C13H20O3	Vomifoliol	[M-H]1-	0.28
E160F00h~E176F00h	224.09	Negative	224.05636	785	224.05672	C11H11N2O2	Tryptophan	[M+Na-2H]1-	-1.61
E114F00h~E480F00h	**228.09**	**Negative**	**227.93053**	**1037**	-	-	**Unknown**	-	-
			228.05118	**403**	**228.05136**	**C9H11NO6**	**4,5-Seco-DOPA**	**[M-H]1-**	**-0.80**
			228.06396	**769**	**228.06421**	**C11H13NO3**	***N*-Acetyl-phenylalanine**	**[M+Na-2H]1-**	**-1.10**
2N=20~2N=30	**229.09**	**Negative**	**228.97551**	**2757**	**228.97561**	**C6H8O7**	**Isocitrate**	**[M+K-2H]1-**	**-0.44**
			228.99346	**1296**	-	-	**Unknown**	-	-
			229.01166	**1801**	**229.01188**	**C5H11O8P**	**Ribose 1-phosphate**	**[M-H]1-**	**-0.97**
E129F00h~E137F00h	**231.09**	**Negative**	**231.03861**	**495**	**231.03873**	**C9H10N2O4**	**N-Carbamoyl-*p*-hydroxy-phenylglycine**	**[M+Na-2H]1-**	**-0.50**
			231.08733	**793**	**231.08741**	**C5H8O3**	**2-Oxo valerate**	**[2M-H]1-**	**-0.36**
			231.09849	**656**	**231.09865**	**C9H16N2O5**	**γ-Glutamyl-γ-aminobutyrate**	**[M-H]1-**	**-0.68**
2N=20~2N=30	**232.09**	**Negative**	**232.01155**	**480**	**232.01048**	**C4H10N3O5P**	**Phospho creatine**	**[M+Na-2H]1-**	**4.62**
E114F00h~E480F00h	**236.09**	**Negative**	**235.97342**	**509**	**235.97318**	**C4H10NO6P**	**O-Phospho homoserine**	**[M+K-2H]1-**	**1.01**
			235.98144	**1156**	-	-	**Unknown**	-	-
E114F00h~E115F00h	**237.09**	**Negative**	**236.95692**	**406**	**236.95720**	**C4H9O7P**	**Erythrose 4-phosphate**	**[M+K-2H]1-**	**-1.17**
			237.00822	**1151**	-	-	**Unknown**	-	-

			237.06160	**1647**	**237.06159**	**C8H14O8**	**3-Deoxy-manno-octulosonate**	**[M-H]1-**	**0.03**
			237.07694	555	237.07685	C12H14O5	3,4,5-Trimethoxy cinnamate	[M-H]1-	0.39
E114F00h~E333F00h	239.09	Negative	239.05898	345	239.05928	C11H12N2O2	Tryptophan	[M+Cl]1-	-1.25
			239.07711	824	239.07724	C4H8O4	Threose	[2M-H]1-	-0.56
E162F00h~E485F00h	**240.09**	**Negative**	**239.95843**	**1747**	**-**	**-**	**Unknown**	**-**	**-**
			239.96779	**855**	**239.96779**	**C7H7O7**	**4-Oxobut-1-ene-1,2,4-tricarboxylate**	**[M+K-2H]1-**	**0.02**
			240.05124	**586**	**240.05136**	**C10H11NO6**	**2,3-Dihydroxy benzoyl serine**	**[M-H]1-**	**-0.51**
E129F00h~E160F00h	**241.09**	**Negative**	**240.97561**	**2333**	**240.97561**	**C7H8O7**	**Oxalo glutarate**	**[M+K-2H]1-**	**0.00**
			241.01201	2478	241.01206	C7H10O7	Homocitrate	[M+Cl]1-	-0.19
E129F00h~E484F00h	**245.09**	**Negative**	**244.93010**	**2022**	**-**	**-**	**Unknown**	**-**	**-**
			245.04323	2492	245.04314	C11H12O5	Sinapate	[M+Na-2H]1-	0.36
			245.05428	625	245.05438	C10H12N2O4	3-Hydroxy kynurenine	[M+Na-2H]1-	-0.39
2N=20~2N=30	**247.09**	**Negative**	**246.97783**	**495**	**246.97782**	**C2H5O4P**	**Phosphono acetaldehyde**	**[2M-H]1-**	**0.04**
			246.99723	**7379**	**246.99605**	**C3H8OS2**	**6-S-Acetyl-dihydro lipoate**	**[2M-H]1-**	**4.78**
			247.01670	**406**	**247.01669**	**C14H10O2**	**Phenanthrene-3,4-diol**	**[M+K-2H]1-**	**0.06**
2N=10~2N=30	**251.18**	**Negative**	**251.05613**	**2649**	**251.05611**	**C6H6O3**	**Maltol**	**[2M-H]1-**	**0.07**
2N=10~2N=30	**253.09**	**Negative**	**252.95123**	**603**	**252.95211**	**C4H9O8P**	**3-Phospho erythronate**	**[M+K-2H]1-**	**-3.49**
			253.07180	**939**	**253.07073**	**C6H15N4O5P**	**N-Phospho arginine**	**[M-H]1-**	**4.22**
			253.09292	519	253.09289	C9H18O8	Galactosyl glycerol	[M-H]1-	0.11
			253.21762	**402**	**253.21730**	**C16H30O2**	**Hexadecenoate**	**[M-H]1-**	**1.25**
E162F00h~E260F00h	**255.27**	**Negative**	**255.08754**	**1199**	**255.08741**	**C12H16O6**	**Phenyl galactoside**	**[M-H]1-**	**0.50**
			255.12372	**765**	**255.12273**	**C12H18N4O**	**Benzoyl agmatine**	**[M+Na-2H]1-**	**3.88**
			255.23299	**2236**	**255.23295**	**C16H32O2**	**Palmitate**	**[M-H]1-**	**0.14**
2N=10~2N=20	**257.08**	**Negative**	**257.00685**	**661**	**257.00680**	**C6H11O9P**	**Glucono-1,5-lactone 6-phosphate**	**[M-H]1-**	**0.21**
			257.03031	**745**	**257.02922**	**C9H8N4O4**	**Xanthopterin-B2**	**[M+Na-2H]1-**	**4.23**
2N=10~2N=20	**259.18**	**Negative**	**259.02271**	**24036**	**259.02245**	**C6H13O9P**	**Glucose 6-phosphate**	**[M-H]1-**	**1.02**
E114F00h~E176F00h	**263.18**	**Negative**	**262.91203**	**1135**	**-**	**-**	**Unknown**	**-**	**-**
			263.05588	**901**	**263.05520**	**C9H14N4O3**	**Carnosine**	**[M+K-2H]1-**	**2.60**
			263.15019	**813**	**263.15001**	**C6H12O3**	**Leucate**	**[2M-H]1-**	**0.67**
E114F00h~E480F00h	**265.18**	**Negative**	264.95243	476	264.95200	C3H8O10P2	Glycerate 1,3-biphosphate	[M-H]1-	1.63
			265.09293	**844**	**265.09182**	**C9H16N4O4**	**Amidino proclavaminate**	**[M+Na-2H]1-**	**4.17**
			265.14791	**6072**	**265.14791**	**C12H26O4S**	**Sodium lauryl sulfate**	**[M-H]1-**	**0.01**
E114F00h~E115F00h	**266.08**	**Negative**	**265.98249**	**824**	**265.98375**	**C5H12NO7P**	**5-Phospho ribosyl amine**	**[M+K-2H]1-**	**-4.73**

			265.99195	1102	-	-	Unknown	-	-
			266.01790	1459	-	-	Unknown	-	-
E260F00h~E484F00h	267.18	Negative	267.01461	1599	-	-	Unknown	-	-
			267.02483	784	267.02513	C6H15O8P	2-Deoxyglucose-6-phosphate	[M+Na-2H]1-	-1.11
			267.07180	1227	267.07216	C9H16O9	Glucosyl glycerate	[M-H]1-	-1.34
E137F00h~E485F00h	269.18	Negative	268.94684	2465	-	-	Unknown	-	-
			269.03362	1109	269.03340	C12H12N2O3	Pheno barbital	[M+K-2H]1-	0.83
			269.24830	549	269.24860	C17H34O2	Methyl palmitate	[M-H]1-	-1.13
2N=20~2N=30	271	Negative	271.00938	1009	-	-	Unknown	-	-
			271.02239	904	271.02256	C9H14O7	(Homo)3-citrate	[M+K-2H]1-	-0.63
2N=10~2N=30	274.08	Negative	273.95757	1335	-	-	Unknown	-	-
			274.03306	464	274.03346	C8H15NO7	N-Acetyl glucosaminate	[M+K-2H]1-	-1.46
2N=20~2N=30	277.18	Negative	277.21765	1726	277.21730	C18H30O2	Linolenate	[M-H]1-	1.25
E114F00h~E137F00h	278.18	Negative	278.06978	1215	278.07018	C13H13N3O2	Methoxy-PU	[M+Cl]1-	-1.43
2N=10~2N=20	279.18	Negative	279.23263	494	279.23295	C18H32O2	Linoleate	[M-H]1-	-1.16
2N=10~2N=20	281.18	Negative	280.98477	1091	280.98341	C6H13O8P	Fucose 1-phosphate	[M+K-2H]1-	4.83
			280.99473	1099	280.99488	C6H12O9S	Glucose 6-sulfate	[M+Na-2H]1-	-0.52
			281.06677	26489	281.06668	C26H28O14	Apigenin 7-*O*-[β-apiosyl-(1->2)-β-glucoside]	[M-2H]2-	0.33
			281.08733	595	281.08781	C10H18O9	Xylobiose	[M-H]1-	-1.70
2N=20~2N=30	289.18	Negative	289.03300	5583	289.03301	C7H15O10P	Sedoheptulose 7-phosphate	[M-H]1-	-0.04
			289.11525	869	289.11536	C10H18N4O6	Arginino succinate	[M-H]1-	-0.38
E480F00h~E485F00h	293.27	Negative	293.02216	741	293.02217	C15H12O4	3',5'-Dihydroxy flavanone	[M+K-2H]1-	-0.02
			293.06675	1960	-	-	Unknown	-	-
E114F00h~E480F00h	295.18	Negative	295.10315	1023	295.10239	C10H18N4O5	N2-Succinyl arginine	[M+Na-2H]1-	2.58
E114F00h~E137F00h	297.18	Negative	297.03549	8420	-	-	Unknown	-	-
			297.06165	10568	297.06159	C13H14O8	Benzoyl glucuronide	[M-H]1-	0.19
			297.15281	5740	-	-	Unknown	-	-
E115F00h~E137F00h	298.18	Negative	298.03371	885	298.03346	C10H15NO7	Hymexazol N-glucoside	[M+K-2H]1-	0.84
			298.15616	1012	-	-	Unknown	-	-
E137F00h~E160F00h	303.18	Negative	302.90814	908	302.90788	C3H8O10P2	Glycerate 1,3-biphosphate	[M+K-2H]1-	0.86
			303.06125	997	303.06134	C10H14N6O3	3'-Amino-3'-deoxyadenosine	[M+K-2H]1-	-0.31
E129F00h~E333F00h	309.18	Negative	308.97803	15770	308.97821	C5H12O11P2	Ribose-1,5-bisphosphate	[M-H]1-	-0.60
			309.11851	1023	-	-	Unknown	-	-

E129F00h~E137F00h	311.18	Negative	311.07690	9334	311.07724	C14H16O8	*O*-Feruloyl threonate	[M-H]1-	-1.10
			311.11357	1030	311.11363	C15H20O7	4-Hydroxycinnamyl alcohol 4-glucoside	[M-H]1-	-0.19
			311.16878	21569	-	-	Unknown	-	-
2N=10~2N=30	312.18	Negative	312.08030	1205	-	-	Unknown	-	-
			312.17183	2433	-	-	13C Isotope of 311.16878	-	-
2N=10~2N=20	315.18	Negative	315.07183	19901	315.07243	C14H16NO6	Indican	[M+Na-2H]1-	-1.91
			315.10845	749	315.10854	C7H10O4	2-Isopropyl maleate	[2M-H]1-	-0.30
2N=10~2N=30	316.18	Negative	316.07486	1936	-	-	13C Isotope of Indican	[M+Na-2H]1-	-
			316.10376	430	316.10272	C12H17N5O4	N6,N6-Dimethyl adenosine	[M+Na-2H]1-	3.28
2N=10~2N=20	319.18	Negative	319.02254	721	319.02241	C16H10O6	2',7-Dihydroxy-4',5'-methylene dioxyisoflavone	[M+Na-2H]1-	0.41
			319.04461	794	319.04594	C15H12O8	2,3-Dihydro quercetagetin	[M-H]1-	-4.18
			319.09060	825	319.08954	C5H8N2O4	Formimino aspartate	[2M-H]1-	3.33
			319.13943	638	319.13984	C14H24O8	Octanoyl glucuronide	[M-H]1-	-1.29
E114F00h~E160F00h	323.18	Negative	323.02805	1327	323.02859	C9H13N2O9P	Uridine monophosphate	[M-H]1-	-1.68
			323.07756	1173	-	-	Unknown	-	-
			323.13409	2537	323.13563	C7H14O2S	7-Mercapto heptanoate	[2M-H]1-	-4.77
E115F00h~E129F00h	326.18	Negative	326.18760	2583	326.18917	C19H31NO	17α-Azahomoandrost-5-en-3β-ol	[M+K-2H]1-	-4.81
E260F00h~E484F00h	327.18	Negative	326.95252	937	326.95251	C6H11O11P	3-Phospho glucarate	[M+K-2H]1-	0.04
			326.98835	786	326.98889	C7H15O10P	Sedoheptulose-7-phosphate	[M+K-2H]1-	-1.66
			327.05765	743	327.05690	C5H8O6	2-Dehydro xylonate	[2M-H]1-	2.28
			327.07158	660	327.07124	C10H18N4O6	Arginino succinate	[M+K-2H]1-	1.04
			327.08849	688	327.08741	C9H8O3	*p*-Coumarate	[2M-H]1-	3.29
			327.21752	1026	327.21770	C18H32O5	9,10,11-Trihydroxy-12,15-octadecadienoate	[M-H]1-	-0.54
E129F00h~E137F00h	329.18	Negative	329.01507	667	329.01562	C9H13N2O8P	dUMP	[M+Na-2H]1-	-1.68
			329.06641	1020	329.06668	C17H14O7	3',4',5-Trihydroxy-3,7-dimethoxyflavone	[M-H]1-	-0.81
			329.23337	686	329.23335	C18H34O5	9,12,13-Trihydroxy-10-octadecenoate	[M-H]1-	0.07
E333F00h~E480F00h	337.09	Negative	337.09263	1224	337.09289	C16H18O8	*p*-Coumaroyl quinate	[M-H]1-	-0.78
E114F00h~E115F00h	340.09	Negative	339.82072	769	-	-	37Cl Isotope of 337.82329	-	-
			340.20246	1783	-	-	Unknown	-	-
2N=20~2N=30	341.27	Negative	341.10886	210747	341.10894	C12H22O11	Sucrose	[M-H]1-	-0.23
2N=20~2N=30	342.18	Negative	342.11240	9428	-	-	13C Isotope of Sucrose	[M-H]1-	-
E114F00h~E115F00h	343.18	Negative	343.11396	1357	-	-	Unknown	-	-
			343.16837	431	343.16810	C19H30O3	5-Androstene-3β,16α,17α-triol	[M+K-2H]1-	0.79

2N=10~2N=20	**344.09**	**Negative**	**344.09872**	**713**	**344.09913**	**C12H23N2O7**	**Fructose lysine**	**[M+K-2H]1-**	**-1.20**
			344.11702	**970**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=20	**346.09**	**Negative**	**346.05500**	**3522**	**346.05581**	**C10H14N5O7P**	**Adenosine monophosphate**	**[M-H]1-**	**-2.34**
			346.09947	**1006**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=30	**347.09**	**Negative**	**346.93344**	**1097**	**346.93410**	**C5H12O11P2**	**Ribose 1,5-bisphosphate**	**[M+K-2H]1-**	**-1.89**
			347.02528	821	347.02560	C6H6O6	Dehydro ascorbate	[2M-H]1-	-0.93
			347.07521	**646**	**347.07484**	**C15H18O8**	***p*-Coumaroyl glucose**	**[M+Na-2H]1-**	**1.07**
			347.17068	763	347.17114	C8H14O4	Suberate	[2M-H]1-	-1.33
E137F00h~E480F00h	**349.09**	**Negative**	349.03274	584	349.03198	C6H16N4O9P2	N-Phospho lombricine	[M-H]1-	2.18
			349.15070	**1518**	**-**	**-**	**Unknown**	**-**	**-**
E129F00h~E160F00h	**355.18**	**Negative**	**355.10285**	**808**	**355.10346**	**C16H20O9**	**1-*O*-Feruloyl glucose**	**[M-H]1-**	**-1.71**
E114F00h~E137F00h	359.18	Negative	359.11957	604	359.11950	C6H12O6	Glucose	[2M-H]1-	0.19
E115F00h~E137F00h	**362.18**	**Negative**	**362.04972**	**960**	**362.05073**	**C10H14N5O8P**	**Guanosine monophosphate**	**[M-H]1-**	**-2.78**
2N=10~2N=30	**364.18**	**Negative**	**364.06671**	**826**	**364.06500**	**C14H17NO9**	**DIBOA-glucoside**	**[M+Na-2H]1-**	**4.69**
			364.11587	**635**	**364.11664**	**C19H21NO5**	**Sinapoyl tyramine**	**[M+Na-2H]1-**	**-2.12**
2N=10~2N=30	**367.18**	**Negative**	**367.10250**	**3571**	**367.10346**	**C17H20O9**	***O*-Feruloyl quinate**	**[M-H]1-**	**-2.61**
2N=10~2N=20	**369.09**	**Negative**	**368.99910**	**1099**	**368.99934**	**C7H16O13P2**	**Sedoheptulose-1,7-bisphosphate**	**[M-H]1-**	**-0.66**
E114F00h~E129F00h	**371.27**	**Negative**	**371.09729**	**7226**	**371.09837**	**C8H10O5**	**2-Hydroxy-3-Ccarboxy-4,5-cyclopropylhex-5-enoate**	**[2M-H]1-**	**-2.92**
			371.13456	650	371.13476	C17H24O9	Syringin	[M-H]1-	-0.53
			371.16320	907	371.16302	C20H30O4	PGA2	[M+K-2H]1-	0.50
2N=10~2N=20	377.27	Negative	377.08556	36887	377.08562	C12H22O11	Sucrose	[M+Cl]1-	-0.15
2N=10~2N=20	**379.18**	**Negative**	**379.04405**	**1081**	**379.04369**	**C15H18O9**	**1-Caffeoyl-β-glucose**	**[M+K-2H]1-**	**0.95**
			379.08156	8368	-	-	37Cl Isotope of Sucrose	[M+Cl]1-	-
			379.15964	**2819**	**379.16097**	**C8H14O5**	**3-Hydroxy suberate**	**[2M-H]1-**	**-3.52**
2N=10~2N=20	**380.18**	**Negative**	**380.04265**	**1257**	**380.04430**	**C20H13N3O3**	**Violacein**	**[M+K-2H]1-**	**-4.33**
2N=10~2N=30	**381.18**	**Negative**	**381.04777**	**737**	**381.04847**	**C10H15N6O6P**	**2-Amino-AMP**	**[M+Cl]1-**	**-1.84**
			381.08684	**552**	**-**	**-**	**Unknown**	**-**	**-**
			381.13136	**592**	**381.13196**	**C20H24O6**	**Lactol**	**[M+Na-2H]1-**	**-1.57**
2N=20~2N=30	**382.18**	**Negative**	**382.01666**	**3079**	**-**	**-**	**Unknown**	**-**	**-**
			382.10196	**652**	**382.10044**	**C14H17N5O8**	**Succinyl adenosine**	**[M-H]1-**	**3.98**
			382.13436	**680**	**382.13549**	**C14H25NO11**	**Galactosyl-3-N-acetyl-β-galactosamine**	**[M-H]1-**	**-2.95**
2N=10~2N=20	**385.18**	**Negative**	**385.11286**	**2095**	**385.11402**	**C17H22O10**	**1-*O*-sinapoyl-β-D-glucose**	**[M-H]1-**	**-3.02**
2N=10~2N=20	**387.18**	**Negative**	**387.11385**	**42068**	**-**	**-**	**Unknown**	**-**	**-**

			387.13057	**740**	**387.12967**	**C17H24O10**	**Verbenalin**	**[M-H]1-**	**2.32**
			387.16508	**881**	**387.16606**	**C18H28O9**	**Tuberonate glucoside**	**[M-H]1-**	**-2.53**
2N=20~2N=30	**388.18**	**Negative**	**388.11613**	**4081**	**388.11679**	**C18H25NO6**	**Anacrotine**	**[M+K-2H]1-**	**-1.71**
			388.11943	**2987**	**-**	**-**	**Unknown**	**-**	**-**
2N=20~2N=30	**389.18**	**Negative**	**389.10703**	**524**	**389.10894**	**C16H22O11**	**Monotropein**	**[M-H]1-**	**-4.90**
			389.11984	790	-	-	13C Isotope of Anacrotine	[M+K-2H]1-	-
			389.14476	**567**	**389.14532**	**C17H26O10**	**Loganin**	**[M-H]1-**	**-1.45**
E137F00h~E162F00h	**393.09**	**Negative**	**393.04432**	**838**	**393.04393**	**C15H16O11**	**2-O-Caffeoyl glucarate**	**[M+Na-2H]1-**	**0.98**
			393.17526	**804**	**393.17555**	**C16H28N4O6**	**(Ac)2-Lys-Ala-Ala**	**[M+Na-2H]1-**	**-0.75**
E115F00h~E485F00h	**397.09**	**Negative**	**397.03990**	**932**	**397.04188**	**C4H10NO6P**	**Phospho threonine**	**[2M-H]1-**	**-4.98**
			397.07609	**2600**	**-**	**-**	**Unknown**	**-**	**-**
			397.07960	**2192**	**397.08074**	**C18H20N2O6**	**Di tyrosine**	**[M+K-2H]1-**	**-2.88**
			397.11394	**829**	**397.11295**	**C17H20N4O6**	**Riboflavin**	**[M+Na-2H]1-**	**2.48**
E114F00h~E115F00h	**398.18**	**Negative**	**398.02072**	**821**	**398.01972**	**C10H19NO10S2**	**3-Hydroxypropyl glucosinolate**	**[M+Na-2H]1-**	**2.53**
			398.08047	**819**	**-**	**-**	**Unknown**	**-**	**-**
			398.13102	**727**	**-**	**-**	**Unknown**	**-**	**-**
E115F00h~E333F00h	**399.18**	**Negative**	**399.01865**	**1071**	**-**	**-**	**Unknown**	**-**	**-**
			399.10657	**672**	**399.10854**	**C21H20O8**	**Flavonol 3-O-galactoside**	**[M-H]1-**	**-4.94**
			399.13059	**832**	**399.12860**	**C17H22N4O6**	**Reduced Riboflavin**	**[M+Na-2H]1-**	**4.98**
2N=10~2N=20	**407.18**	**Negative**	**407.06487**	**1374**	**-**	**-**	**Unknown**	**-**	**-**
			407.15687	**739**	**407.15676**	**C9H16O3S**	**2-Oxo-8-methyl thiooctanoate**	**[2M-H]1-**	**0.27**
			407.19153	**913**	**407.19227**	**C9H16O5**	**Diethyl-2-methyl-3-hydroxy succinate**	**[2M-H]1-**	**-1.82**
2N=10~2N=30	**408.09**	**Negative**	**407.78586**	**835**	**-**	**-**	**Unknown**	**-**	**-**
			408.14996	**688**	**408.15114**	**C16H27NO11**	**Linustatin**	**[M-H]1-**	**-2.88**
E114F00h~E137F00h	**413.18**	**Negative**	**413.08269**	**1090**	**-**	**-**	**Unknown**	**-**	**-**
			413.14330	**3219**	**413.14305**	**C8H17NOS2**	**Dihydro lipoamide**	**[2M-H]1-**	**0.61**
			413.21669	**530**	**-**	**-**	**Unknown**	**-**	**-**
E480F00h~E485F00h	**419.09**	**Negative**	419.09701	1150	419.09837	C10H10O5	5-Hydroxy ferulate	[2M-H]1-	-3.25
			419.11131	**748**	**419.11191**	**C15H22N6O5S**	**S-Adenosyl methionine**	**[M+Na-2H]1-**	**-1.43**
			419.15588	**717**	**-**	**-**	**Unknown**	**-**	**-**
			419.19186	**833**	**-**	**-**	**Unknown**	**-**	**-**
E333F00h~E480F00h	**420.18**	**Negative**	**420.09271**	**936**	**420.09137**	**C14H25NO11**	**β-1,4-Mannose-N-acetyl glucosamine**	**[M+K-2H]1-**	**3.19**
E137F00h~E162F00h	**421.18**	**Negative**	**421.07450**	**959**	**421.07527**	**C12H23O14P**	**Sucrose 6-phosphate**	**[M-H]1-**	**-1.83**

			421.15300	**797**	**-**	**-**	**Unknown**	**-**	**-**
2N=20~2N=30	**423.18**	**Negative**	**423.15902**	**755**	**423.16018**	**C14H12O2**	**Phenanthrene-9,10-dihydrodiol**	**[2M-H]1-**	**-2.75**
			423.16439	**721**	**-**	**-**	**Unknown**	**-**	**-**
			423.17750	**569**	**-**	**-**	**Unknown**	**-**	**-**
2N=20~2N=30	**425.18**	**Negative**	**425.06861**	**872**	**-**	**-**	**Unknown**	**-**	**-**
			425.08145	**634**	**425.08064**	**C13H22N4O8S2**	**S-Glutathionyl cysteine**	**[M-H]1-**	**1.91**
			425.18283	**366**	**425.18171**	**C21H30O9**	**Abscisate glucose ester**	**[M-H]1-**	**2.64**
E114F00h~E480F00h	**427.18**	**Negative**	**427.02514**	**981**	**-**	**-**	**Unknown**	**-**	**-**
			427.15953	**827**	**427.16097**	**C20H28O10**	**Furcatin**	**[M-H]1-**	**-3.38**
E176F00h~E484F00h	**429.18**	**Negative**	**429.01887**	**1017**	**429.01698**	**C14H18NO9S2**	**Benzyl glucosinolate**	**[M+Na-2H]1-**	**4.42**
			429.10258	**1004**	**429.10448**	**C5H14NO6P**	**1-Glycero phosphoryl ethanolamine**	**[2M-H]1-**	**-4.42**
E160F00h~E485F00h	**431.18**	**Negative**	431.09630	3091	431.09837	C21H20O10	Apigenin 7-O-β-Glucoside	[M-H]1-	-4.81
			431.10226	**3774**	**-**	**-**	**Unknown**	**-**	**-**
			431.21946	**657**	**431.21801**	**C19H39O7P**	**PA(16:0/0:0)[U]**	**[M+Na-2H]1-**	**3.36**
2N=10~2N=20	**435.18**	**Negative**	**434.88340**	**1038**	**-**	**-**	**Unknown**	**-**	**-**
			435.09079	**2048**	**435.09088**	**C18H22O11**	**Asperuloside**	**[M+Na-2H]1-**	**-0.21**
			435.22173	654	435.22357	C10H18O5	3-Hydroxy sebacate	[2M-H]1-	-4.23
2N=10~2N=20	**437.18**	**Negative**	**437.07430**	**1854**	**437.07451**	**C6H10N3O4P**	**Hydroxymethyl pyrimidine phosphate**	**[2M-H]1-**	**-0.49**
			437.16579	**680**	**-**	**-**	**Unknown**	**-**	**-**
			437.20118	**733**	**-**	**-**	**Unknown**	**-**	**-**
E115F00h~E129F00h	**440.18**	**Negative**	**440.07767**	**2101**	**-**	**-**	**Unknown**	**-**	**-**
			440.08685	**4486**	**-**	**-**	**Unknown**	**-**	**-**
E114F00h~E480F00h	**443.18**	**Negative**	**443.11784**	**941**	**-**	**-**	**Unknown**	**-**	**-**
			443.15395	**769**	**443.15588**	**C19H22N7O6**	**7,8-Dihydrofolate**	**[M-H]1-**	**-4.36**
			443.19239	**595**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=20	**447.18**	**Negative**	**447.09066**	**5773**	**-**	**-**	**Unknown**	**-**	**-**
			447.11578	**661**	**-**	**-**	**Unknown**	**-**	**-**
			447.13322	**1139**	**-**	**-**	**Unknown**	**-**	**-**
			447.15353	954	447.15214	C10H12N2O4	3-Hydroxy kynurenine	[2M-H]1-	3.11
E114F00h~E480F00h	449.09	Negative	449.10829	750	449.10894	C21H22O11	Pentahydroxychalcone 4'-O-glucoside	[M-H]1-	-1.44
E129F00h~E137F00h	**453.18**	**Negative**	453.07977	983	453.08032	C21H20O10	Apigenin 7-O-β-Glucoside	[M+Na-2H]1-	-1.21
			453.10262	**1018**	**-**	**-**	**Unknown**	**-**	**-**
			453.15216	**339**	**453.15147**	**C10H13NO5**	**Arogenate**	**[2M-H]1-**	**1.52**

2N=20~2N=30	**455.18**	**Negative**	**455.09684**	**968**	**455.09734**	**C17H21N4O9P**	**Flavin Mononucleotide**	**[M-H]1-**	**-1.10**
			455.11768	**466**	**-**	**-**	**Unknown**	**-**	**-**
			455.19400	**497**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=30	**459.09**	**Negative**	**459.14936**	**733**	**459.15080**	**C20H28O12**	**Paeonolide**	**[M-H]1-**	**-3.14**
E129F00h~E160F00h	**463.18**	**Negative**	**463.04259**	**1168**	**-**	**-**	**Unknown**	**-**	**-**
			463.21764	**700**	**463.21936**	**C11H20O3S**	**2-Oxo-10-Methylthiodecanoate**	**[2M-H]1-**	**-3.72**
2N=10~2N=30	469.18	Negative	469.07361	731	469.07523	C21H20O11	Kaempferol 7-O-Glucoside	[M+Na-2H]1-	-3.46
Pilar analysis	**471.18**	**Negative**	**471.07287**	**1714**	**-**	**-**	**Unknown**	**-**	**-**
			471.09209	639	471.09088	C21H22O11	Pentahydroxychalcone 4'-O-Glucoside	[M+Na-2H]1-	2.56
			471.07287	**1714**	**-**	**-**	**Unknown**	**-**	**-**
2N=20~2N=30	**475.09**	**Negative**	475.12810	1774	475.13046	C8H14O8	3-Deoxy-manno-octulosonate	[2M-H]1-	-4.97
			475.14890	**1095**	**-**	**-**	**Unknown**	**-**	**-**
			475.21772	641	475.21608	C20H38O11	Octyl β-1,6-galactofuranosyl-α-glucopyranoside	[M+Na-2H]1-	3.44
E115F00h~E485F00h	**479.18**	**Negative**	**479.03946**	**585**	**479.04044**	**C6H12N2O4S2**	**Cystine**	**[2M-H]1-**	**-2.04**
			479.10104	**664**	**479.09971**	**C13H8N2O3**	**2-Hydroxyphenazine-1-carboxylate**	**[2M-H]1-**	**2.78**
E114F00h~E137F00h	**481.27**	**Negative**	**481.25439**	**1224**	**481.25720**	**C22H43O9P**	**2-16:1-LysoPG**	**[M-H]1-**	**-5.83**
2N=10~2N=30	**483.27**	**Negative**	**483.27087**	**1074**	**483.27285**	**C22H45O9P**	**PG(16:0/0:0)**	**[M-H]1-**	**-4.09**
2N=10~2N=30	**487.18**	**Negative**	**487.15628**	**647**	**487.15592**	**C14H29N6O11P**	**O-1,4-α-Dihydrostreptosyl-streptidine 6-phosphate**	**[M-H]1-**	**0.74**
			487.17619	**2177**	**487.17516**	**C28H26N4O3**	**Staurosporine**	**[M+Na-2H]1-**	**2.12**
2N=10~2N=20	**488.18**	**Negative**	**488.06261**	**2308**	**-**	**-**	**Unknown**	**-**	**-**
			488.10807	**663**	**488.10957**	**C18H23N6O7S**	**(4-Azidophenacyl)glutathione**	**[M+Na-2H]1-**	**-3.06**
			488.15921	**3655**	**-**	**-**	**Unknown**	**-**	**-**
			488.18137	**1209**	**-**	**-**	**Unknown**	**-**	**-**
E114F00h~E484F00h	**493.18**	**Negative**	**493.12949**	**565**	**493.13113**	**C9H13NO7**	**N-Succinyl glutamate**	**[2M-H]1-**	**-3.33**
E114F00h~E480F00h	503.27	Negative	503.15904	1878	503.16176	C18H32O16	Raffinose	[M-H]1-	-5.41
2N=10~2N=20	**510**	**Negative**	**510.10117**	**545**	**510.10193**	**C20H27NO12**	**Proteacin**	**[M+K-2H]1-**	**-1.50**
			510.21737	**537**	**510.21672**	**C25H37NO8S**	**ω-carboxy-N-acetyl-Lte4**	**[M-H]1-**	**1.28**
2N=10~2N=30	513.17	Negative	513.10357	830	513.10145	C23H24O12	Cicerin-7-O-glucoside	[M+Na-2H]1-	4.14
2N=20~2N=30	**515.17**	**Negative**	**515.10021**	**1036**	**515.09837**	**C14H10O5**	**Gentisin**	**[2M-H]1-**	**3.57**
			515.12404	**1005**	**-**	**-**	**Unknown**	**-**	**-**
E115F00h~E176F00h	521	Negative	521.33212	758	521.33312	C26H50O10	Tween 20	[M-H]1-	-1.92
E115F00h~E485F00h	**534.09**	**Negative**	**534.17408**	**1007**	**534.17455**	**C27H31NO9**	**13-Deoxydaunorubicin**	**[M+Na-2H]1-**	**-0.88**
E333F00h~E480F00h	**535.27**	**Negative**	**535.03503**	**1020**	**535.03719**	**C14H22N2O16P2**	**UDP-Arabinose**	**[M-H]1-**	**-4.03**

E114F00h~E137F00h	539.27	Negative	539.13550	2797	539.13844	C18H32O16	Raffinose	[M+Cl]1-	-5.45
E114F00h~E137F00h	**540.17**	**Negative**	**540.03362**	**1018**	**-**	**-**	**Unknown**	**-**	**-**
			540.05642	**1055**	**540.05384**	**C15H21N5O13P2**	**Cyclic ADP-ribose**	**[M-H]1-**	**4.78**
E137F00h~E160F00h	541.27	Negative	541.13280	1033	-	-	37Cl Isotope of raffinose	[M+Cl]1-	-
2N=10~2N=20	563.27	Negative	563.13800	6060	563.14063	C26H28O14	Apigenin 7-O-[β-apiosyl-(1->2)-β-glucoside]	[M-H]1-	-4.68
2N=10~2N=20	564.27	Negative	564.14164	1829	-	-	13C Isotope of Apigenin 7-O-[β-apiosyl-(1->2)-β-glucoside]	[M-H]1-	-
E480F00h~E485F00h	**565.17**	**Negative**	**565.04434**	**2039**	**-**	**-**	**Unknown**	**-**	**-**
			565.14542	**770**	**565.14816**	**C28H32O10**	**1,2-Bis-O-sinapoyl-β-glucoside**	**[M+K-2H]1-**	**-4.84**
E114F00h~E137F00h	**566.27**	**Negative**	**566.04925**	**1087**	**-**	**-**	**Unknown**	**-**	**-**
			566.15362	**3011**	**566.15604**	**C27H31O11**	**Curcumin monoglucoside**	**[M+Cl]1-**	**-4.28**
E137F00h~E162F00h	567.17	Negative	567.15793	810	-	-	13C Isotope of Curcumin monoglucoside	[M+Cl]1-	-
2N=10~2N=30	**588.09**	**Negative**	**588.07437**	**566**	**588.07497**	**C16H25N5O15P2**	**ADP-Glucose**	**[M-H]1-**	**-1.02**
			588.13461	**934**	**588.13651**	**C19H33N3O14P2**	**dTDP-4-dimethylamino-4,6-dideoxy-5-C-methyl-mannose**	**[M-H]1-**	**-3.22**
E114F00h~E137F00h	**593.27**	**Negative**	**593.15028**	**1107**	**593.15120**	**C27H30O15**	**Isoorientin 2''-*O*-rhamnoside**	**[M-H]1-**	**-1.55**
2N=20~2N=30	**597.17**	**Negative**	**597.21676**	**708**	**597.21951**	**C10H22NO7P**	**PC(0:0/2:0)**	**[2M-H]1-**	**-4.60**
2N=20~2N=30	**601.17**	**Negative**	**601.13443**	**1974**	**601.13290**	**C27H32O13**	**Pinocembrin 7-rhamnosyl glucoside**	**[M+K-2H]1-**	**2.55**
2N=10~2N=20	**623.17**	**Negative**	**623.18176**	**1037**	**623.18316**	**C25H30N8O10**	**10-Formyl tetrahydrofolyl Glutamate**	**[M+Na-2H]1-**	**-2.25**
Pilar analysis	**637.09**	**Negative**	**637.17555**	**497**	**637.17741**	**C29H34O16**	**Dalpatein 7-O-β-D-apiofuranosyl-(1->6)-β-D-glucopyranoside**	**[M-H]1-**	**-2.92**
2N=20~2N=30	**640.9**	**Negative**	**641.12809**	**1069**	**-**	**-**	**Unknown**	**-**	**-**
			641.20676	**493**	**641.20644**	**C13H23NO4S2**	**Glutaryl dihydro lipoamide**	**[2M-H]1-**	**0.50**
E129F00h~E176F00h	683.27	Negative	683.22272	1119	683.22515	C12H22O11	Sucrose	[2M-H]1-	-3.56
2N=10~2N=20	711.45	Negative	711.21064	847	711.21419	C16H20O9	1-O-Feruloyl-β-glucose	[2M-H]1-	-5.00
2N=10~2N=20	**719.63**	**Negative**	**719.48650**	**618**	**719.48686**	**C38H73O10P**	**PG(16:0/16:1(9Z))**	**[M-H]1-**	**-0.50**
E115F00h~E129F00h	741.63	Negative	741.46610	2498	741.46881	C38H73O10P	PG(16:0/16:1(9Z))	[M+Na-2H]1-	-3.65
E137F00h~E480F00h	**743.63**	**Negative**	**743.48374**	**844**	**743.48686**	**C40H73O10P**	**PG(16:0/18:3(6Z,9Z,12Z))**	**[M-H]1-**	**-4.20**
			743.79062	**700**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=30	**745.63**	**Negative**	**745.50062**	**438**	**745.50251**	**C40H75O10P**	**PG(18:1(11Z)/16:1(9Z))**	**[M-H]1-**	**-2.54**
E115F00h~E129F00h	**773.36**	**Negative**	**773.26046**	**852**	**-**	**-**	**Unknown**	**-**	**-**
			773.52328	363	773.52092	C45H74O10	1,2 Di-(9Z,12Z,15Z-Octadecatrienoyl)-3-O-β-galactosyl-sn-glycerol	[M-H]1-	3.05
E115F00h~E137F00h	**793.72**	**Negative**	**793.51235**	**340**	**793.51413**	**C41H78O12S**	**1,2-Dihexadecanoyl-3-(6'-sulfo-α-D-quinovosyl)-sn-glycerol**	**[M-H]1-**	**-2.24**
2N=10~2N=20	**815.72**	**Negative**	**815.49378**	**1974**	**815.49510**	**C23H36O6**	**15R-PGE2 methyl ester, 15-acetate**	**[2M-H]1-**	**-1.62**
2N=10~2N=30	**819.63**	**Negative**	**819.52028**	**683**	**819.51816**	**C46H77O10P**	**PG(18:1(11Z)/22:6(4Z,7Z,10Z,13Z,16Z,19Z))**	**[M-H]1-**	**2.59**
2N=10~2N=20	**831.63**	**Negative**	**831.50131**	**1049**	**831.50291**	**C43H77O13P**	**1-16:0-2-18:3-Phosphatidyl inositol**	**[M-H]1-**	**-1.92**

2N=10~2N=20	**837.63**	**Negative**	**837.51583**	**1378**	**837.51343**	**C47H76O11**	**1-(9Z-Octadecenoyl)-2-(5Z,8Z,11Z,14Z-eicosatetraenoyl)-3-O-α-glucuronyl-sn-glycerol**	**[M+Na-2H]1-**	**2.86**
E129F00h~E176F00h	58.09	Positive	58.06525	105784	58.06513	C4H9NO2	γ-Amino butyrate	[M+H-FA]1+	2.07
E115F00h~E137F00h	**62.09**	**Positive**	62.02391	573	62.02366	CH3NO2	Carbamate	[M+H]1+	4.11
			62.06016	**8197**	**62.06004**	**C2H7NO**	**Ethanol amine**	**[M+H]1+**	**1.84**
E176F00h~E485F00h	**74.09**	**Positive**	**74.02360**	**2574**	**74.02366**	**C2H3NO2**	**Imino glycine**	**[M+H]1+**	**-0.77**
			74.06000	**11367**	**74.06004**	**C3H7NO**	**3-Amino propanal**	**[M+H]1+**	**-0.53**
			74.09637	**22483**	**74.09643**	**C4H11N**	**Butyl amine**	**[M+H]1+**	**-0.74**
E137F00h~E162F00h	**84.09**	**Positive**	**84.03311**	**5931**	**-**	**-**	**Unknown**	**-**	**-**
			84.08072	**58124**	**84.08078**	**C5H9N**	**Piperideine**	**[M+H]1+**	**-0.63**
Pilar analysis	**98**	**Positive**	**98.05794**	**1559**	**98.05764**	**C3H9NO**	**1-Amino propan-2-ol**	**[M+Na]1+**	**3.14**
E115F00h~E480F00h	**102**	**Positive**	**102.03358**	**117144**	**-**	**-**	**Unknown**	**-**	**-**
			102.05467	**21923**	**102.05496**	**C4H7NO2**	**Aceto acetamide**	**[M+H]1+**	**-2.80**
			102.05637	**23625**	**-**	**-**	**Unknown**	**-**	**-**
			102.09102	**2493**	**102.09134**	**C5H11NO**	**5-Amino pentanal**	**[M+H]1+**	**-3.14**
E114F00h~E480F00h	**106**	**Positive**	**106.04956**	**63524**	**106.04987**	**C3H7NO3**	**Serine**	**[M+H]1+**	**2.46**
			106.05803	**6506**	**-**	**-**	**Unknown**	**-**	**-**
E115F00h~E260F00h	**107**	**Positive**	**107.04871**	**1150**	**107.04914**	**C7H6O**	**Benzaldehyde**	**[M+H]1+**	**-4.04**
			107.05285	1342	-	-	13C Isotope of Serine	[M+H]1+	-
			107.05749	**4891**	**-**	**-**	**Unknown**	**-**	**-**
2N=20~2N=30	**111.54**	**Positive**	**111.55769**	**16203**	**111.55786**	**C7H15N3O5**	**1-Guanidino-1-deoxy-scyllo-inositol**	**[M+2H]2+**	**-1.55**
E115F00h~E176F00h	**113.45**	**Positive**	**113.54643**	**6717**	**-**	**-**	**Unknown**	**-**	**-**
			113.55113	**608**	**113.55104**	**C10H13N2O4**	**Porphobilinogen**	**[M+2H]2+**	**0.77**
2N=10~2N=20	**114**	**Positive**	**114.01677**	**8539**	**-**	**-**	**Unknown**	**-**	**-**
			114.03965	**53325**	**-**	**-**	**Unknown**	**-**	**-**
			114.05459	**1861**	**114.05496**	**C5H7NO2**	**Pyrroline 5-carboxylate**	**[M+H]1+**	**-3.21**
			114.06571	**1627**	**114.06619**	**C4H7N3O**	**Creatinine**	**[M+H]1+**	**-4.20**
E114F00h~E176F00h	**116**	**Positive**	**116.03384**	**2969**	**116.03422**	**C4H5NO3**	**Maleamate**	**[M+H]1+**	**-3.28**
			116.03719	4024	-	-	41K Isotope of 114.03965	-	-
			116.07030	**9205**	**116.07061**	**C5H9NO2**	**Proline**	**[M+H]1+**	**-2.64**
2N=20~2N=30	**118.09**	**Positive**	**118.08587**	**1468640**	**118.08626**	**C5H11NO2**	**Valine and Betaine**	**[M+H]1+**	**-3.27**
2N=20~2N=30	**119.09**	**Positive**	**119.06990**	**1033**	**119.07027**	**C5H10O3**	**2-Hydroxy valerate**	**[M+H]1+**	**-3.12**
			119.08914	61037	-	-	13C Isotope of Valine and 13C Isotope of Betaine	[M+H]1+	-

E115F00h~E260F00h	**120.09**	**Positive**	**120.06515**	**37635**	**120.06552**	**C4H9NO3**	**Threonine**	**[M+H]1+**	**-3.09**
2N=20~2N=30	**123**	**Positive**	**122.92412**	**91633**	**-**	**-**	**Unknown**	**-**	**-**
			123.03989	**16616**	**123.04004**	**CH3NO2**	**Carbamate**	**[2M+H]1+**	**-1.18**
			123.05488	**1942**	**123.05529**	**C6H6N2O**	**Nicotinamide**	**[M+H]1+**	**-3.33**
			123.06563	**1708**	**123.06519**	**C4H10O4**	**Erythritol**	**[M+H]1+**	**3.60**
			123.07052	**14008**	**-**	**-**	**Unknown**	**-**	**-**
E114F00h~E137F00h	**123.9**	**Positive**	124.06019	1635	124.06044	C3H6O4	Glycerate	[M+NH4]1+	-1.98
			124.07274	**1141**	**124.07329**	**C5H11NO**	**4-Methyl aminobutanal**	**[M+Na]1+**	**-4.39**
			124.07524	**949**	**124.07569**	**C7H9NO**	**2-Amino-*m*-cresol**	**[M+H]1+**	**-3.63**
E129F00h~E162F00h	**127.09**	**Positive**	**126.99838**	**1561**	**126.99783**	**C4H8S**	**Tetrahydro thiophene**	**[M+K]1+**	**4.31**
			127.03856	**1568**	**127.03897**	**C6H6O3**	**1,2,3-Trihydroxy benzene**	**[M+H]1+**	**-3.24**
			127.05142	**1408**	**127.05197**	**C5H12O**	**2-Methyl butanol**	**[M+K]1+**	**-4.36**
			127.12251	**69695**	**127.12298**	**C7H14N2**	**1,5-Diazabicyclo nonane**	**[M+H]1+**	**-3.66**
E137F00h~E162F00h	**128**	**Positive**	**128.01035**	**1790**	**128.01084**	**C3H7NO2**	**Alanine**	**[M+K]1+**	**-3.81**
			128.03128	1312	128.03182	C3H7NO3	Serine	[M+Na]1+	-4.18
			128.05521	**10759**	**-**	**-**	**Unknown**	**-**	**-**
			128.12580	2467	-	-	13C Isotope of 1,5-Diazabicyclo nonane	[M+H]1+	-
E115F00h~E176F00h	**132**	**Positive**	**132.06510**	**1328**	**132.06552**	**C5H9NO3**	**3-Hydroxy proline**	**[M+H]1+**	**-3.19**
			132.10146	**21097**	**132.10191**	**C6H13NO2**	**Leucine**	**[M+H]1+**	**-3.38**
2N=20~2N=30	132.44	Positive	132.54472	2360	132.54456	C9H17NO5	Pantothenate	[M+2Na]2+	1.22
2N=20~2N=30	**138.09**	**Positive**	**138.03123**	**1982**	**138.03157**	**C5H9NO**	**N-Methyl-2-pyrrolidinone**	**[M+K]1+**	**-2.48**
			138.05268	995	138.05255	C5H9NO2	Proline	[M+Na]1+	0.94
			138.05463	**26472**	**138.05496**	**C7H7NO2**	**4-Amino benzoate**	**[M+H]1+**	**-2.36**
			138.06632	**4438**	**138.06619**	**C6H7N3O**	**6-Amino nicotinamide**	**[M+H]1+**	**0.95**
			138.09106	**3707**	**138.09134**	**C8H11NO**	**Tyramine**	**[M+H]1+**	**-2.03**
E114F00h~E333F00h	**139**	**Positive**	**139.03864**	**1298**	**139.03897**	**C7H6O3**	**Salicylate**	**[M+H]1+**	**-2.39**
			139.04997	**6643**	**139.05021**	**C6H6N2O2**	**Urocanate**	**[M+H]1+**	**-1.69**
			139.06314	**5781**	**-**	**-**	**Unknown**	**-**	**-**
			139.08628	**1429**	**139.08659**	**C7H10N2O**	**4-Hydroxymethyl phenyl hydrazine**	**[M+H]1+**	**-2.23**
E114F00h~E137F00h	**139.9**	**Positive**	**140.06789**	**56514**	**140.06820**	**C5H11NO2**	**Betaine**	**[M+Na]1+**	**-2.21**
E160F00h~E260F00h	**141**	**Positive**	**141.00604**	**1011**	**141.00609**	**C3H6N2O2**	**N-Formimino glycine**	**[M+K]1+**	**-0.33**
			141.07129	1728	-	-	13C Isotope of Betaine	[M+Na]1+	-
2N=10~2N=20	**141.9**	**Positive**	142.02611	662	142.02649	C4H9NO2	γ-Amino butyrate	[M+K]1+	-2.66

			142.03462	**287089**	**142.03462**	**CH2O3**	**Carbonate**	**[2M+NH4]1+**	**0.03**
			142.04697	706	142.04747	C4H9NO3	Threonine	[M+Na]1+	-3.48
			142.09690	**1118**	**142.09749**	**C6H11N3O**	**Histidinol**	**[M+H]1+**	**-4.15**
E137F00h~E160F00h	**144**	**Positive**	144.00543	2431	144.00575	C3H7NO3	Serine	[M+K]1+	-2.24
			144.03214	**27607**	**144.03251**	**C2H6O4S**	**2-Hydroxy ethane sulfonate**	**[M+NH4]1+**	**-2.57**
			144.06523	1004	144.06552	C6H11NO4	2-Amino adipate	[M+H-H2O]1+	-2.02
			144.07818	**1793**	**144.07837**	**C8H11N**	**2,4-Dimethyl aniline**	**[M+Na]1+**	**-1.32**
			144.08048	**5912**	**144.08078**	**C10H9N**	**3-Methyl quinoline**	**[M+H]1+**	**-2.05**
			144.10153	**1015**	**144.10191**	**C7H13NO2**	**Proline Betaine**	**[M+H]1+**	**-2.61**
E115F00h~E333F00h	**145**	**Positive**	**144.99260**	**2258**	**144.99299**	**C3H6O3S**	**3-Mercapto lactate**	**[M+Na]1+**	**-2.69**
			145.02584	2258	145.02600	C7H6O2	Benzoate	[M+Na]1+	-1.11
			145.04925	**1706**	**145.04954**	**C6H8O4**	**2,3-Dimethyl maleate**	**[M+H]1+**	**-1.98**
			145.08565	**518**	**145.08592**	**C7H12O3**	**5-Aceto valerate**	**[M+H]1+**	**-1.87**
2N=10~2N=30	**147.09**	**Positive**	**147.07615**	**144700**	**147.07642**	**C5H10N2O3**	**Glutamine**	**[M+H]1+**	**-1.84**
			147.11243	**3326**	**147.11281**	**C6H14N2O2**	**Lysine**	**[M+H]1+**	**-2.55**
2N=20~2N=30	**149.54**	**Positive**	**149.51780**	**619**	**149.51854**	**C11H11NO6**	**N-Pyruvoyl-5-methoxy-3-hydroxy anthranilate**	**[M+2Na]2+**	**-4.96**
E115F00h~E129F00h	**150**	**Positive**	**150.02434**	**8246**	**-**	**-**	**Unknown**	**-**	**-**
			150.05205	**1418**	**150.05255**	**C6H9NO2**	**N-Ethyl succinimide**	**[M+Na]1+**	**-3.33**
			150.05785	**1306**	**150.05833**	**C5H11NO2S**	**Methionine**	**[M+H]1+**	**-3.20**
			150.07716	**1562**	**150.07742**	**C6H7N5**	**1-Methyl adenine**	**[M+H]1+**	**-1.75**
E114F00h~E176F00h	156	Positive	156.04174	2193725	156.04214	C5H11NO2	Betaine	[M+K]1+	-2.54
E114F00h~E176F00h	157	Positive	157.01040	4940	157.01075	C4H6O5	Malate	[M+Na]1+	-2.20
			157.04508	104241	-	-	13C Isotope of Betaine	[M+K]1+	-
E114F00h~E176F00h	158	Positive	158.03993	147095	-	-	41K Isotope of Betaine	[M+K]1+	-
E114F00h~E162F00h	**159**	**Positive**	**159.00825**	**3883**	**159.00864**	**C4H8O3S**	**Methyl-1-thio-glycerate**	**[M+Na]1+**	**-2.45**
			159.02003	**1170**	**159.02056**	**C6H7O3P**	**Phenyl phosphonate**	**[M+H]1+**	**-3.33**
			159.04318	4912	-	-	41K Isotope of 13C isotope of Betaine	[M+K]1+	-
			159.06298	**1940**	**159.06278**	**C5H12O4**	**Apiitol**	**[M+Na]1+**	**1.25**
			159.06496	827	159.06519	C7H10O4	2-Isopropyl maleate	[M+H]1+	-1.43
			159.07608	**4776**	**159.07642**	**C6H10N2O3**	**4-Methylene glutamine**	**[M+H]1+**	**-2.14**
E480F00h~E485F00h	**160**	**Positive**	160.03656	1355	160.03690	C7H7NO2	4-Amino benzoate	[M+Na]1+	-2.12
			160.06008	**1272**	**160.06044**	**C6H9NO4**	**N-Methyl-2-oxoglutaramate**	**[M+H]1+**	**-2.22**
			160.07530	**1823**	**160.07569**	**C10H9NO**	**Indole-3-acetaldehyde**	**[M+H]1+**	**-2.44**

			160.08147	15032	-	-	Unknown	-	-
			160.09642	580	160.09682	C7H13NO3	3-Dehydro carnitine	[M+H]1+	-2.50
E114F00h~E160F00h	161	Positive	160.99587	1006	160.99592	CH3NO2	Carbamate	[2M+K]1+	-0.29
			161.05636	1703	161.05569	C5H8N2O4	N-Formimino aspartate	[M+H]1+	4.19
			161.09172	15738	161.09207	C6H12N2O3	Alanyl alanine	[M+H]1+	-2.17
			161.10691	2696	161.10733	C10H12N2	Tryptamine	[M+H]1+	-2.58
2N=20~2N=30	173	Positive	172.98404	10630	172.98468	C4H6O5	Malate	[M+K]1+	-3.72
			173.02061	987	173.02096	C3H9O6P	Glycerol 3-phosphate	[M+H]1+	-1.99
			173.05689	5698	173.05730	C9H10O2	4-Coumaryl alcohol	[M+Na]1+	-2.37
			173.09153	1075	173.09207	C7H12N2O3	Glycyl proline	[M+H]1+	-3.12
2N=20~2N=30	175	Positive	174.89537	108998	174.89594	H3O4P	Phosphate	[M+2K-H]1+	-3.25
			174.98220	1969	-	-	41K Isotope of Malate	[M+K]1+	-
			174.99951	1388	175.00033	C4H8O5	Erythronate	[M+K]1+	-4.71
			175.10717	2176	175.10772	C7H14N2O3	N-Acetyl ornithine	[M+H]1+	-3.14
			175.11843	11805	175.11895	C6H14N4O2	Arginine	[M+H]1+	-2.99
E115F00h~E137F00h	176	Positive	176.01021	48076	176.01084	C7H7NO2	2-Amino benzoate	[M+K]1+	-3.57
			176.02235	1109	176.02207	C6H7N3O	6-Amino nicotinamide	[M+K]1+	1.59
			176.05801	10255	176.05846	C7H11N3	2,4,6-Triamino toluene	[M+K]1+	-2.53
			176.09119	2036	176.09174	C7H13NO4	α-Amino pimelate	[M+H]1+	-3.10
			176.10230	16727	176.10297	C6H13N3O3	Argininate	[M+H]1+	-3.80
E115F00h~E129F00h	182	Positive	182.08037	1542	182.08117	C9H11NO3	Tyrosine	[M+H]1+	-4.40
E114F00h~E162F00h	183.09	Positive	182.94488	2026	182.94565	C3H6O4	Glycerate	[M+2K-H]1+	-4.21
			183.06088	49094	-	-	Unknown	-	-
			183.10088	1107	183.10157	C10H14O3	Dihydro coniferyl alcohol	[M+H]1+	-3.78
			183.11210	1295	183.11281	C9H11NO2	Phenylalanine	[M+NH4]1+	-3.85
E114F00h~E137F00h	184	Positive	184.03635	2037	184.03705	C6H11NO3	5-Hydroxy pipecolate	[M+K]1+	-3.81
			184.05752	738	184.05803	C6H11NO4	2-Amino adipate	[M+Na]1+	-2.77
			184.06423	2412	184.06381	C5H13NO4S	Choline sulfate	[M+H]1+	2.28
			184.07264	3572	184.07344	C7H15NO2	3-Dehydroxy carnitine	[M+K]1+	-4.34
2N=10~2N=20	185.09	Positive	185.00535	8688	185.00566	C5H6O6	4-Hydroxy-2-oxoglutarate	[M+Na]1+	-1.68
			185.02027	957	185.02107	C6H10O4	Adipate	[M+K]1+	-4.32
			185.03161	192517	185.03230	C5H10N2O3	Glutamine	[M+K]1+	-3.73
			185.04130	1213	185.04205	C6H10O5	3,3-Dimethyl malate	[M+Na]1+	-4.03

			185.06809	1045	185.06869	C6H14N2O2	Lysine	[M+K]1+	-3.23
E115F00h~E137F00h	187.09	Positive	186.99946	1498	187.00022	C3H7O7P	3-Phosphoglycerate	[M+H]1+	-4.06
			187.02959	6927	-	-	41K Isotope of Glutamine	[M+K]1+	-
			187.03591	1520	187.03657	C9H8O3	*p*-Coumarate	[M+Na]1+	-3.51
Pilar analysis	**188.09**	**Positive**	**188.01373**	**2659**	**188.01421**	**C5H11NO2S**	**L-Methionine**	**[M+K]1+**	**-2.56**
			188.06743	**918**	**188.06820**	**C9H11NO2**	**L-Phenylalanine**	**[M+Na]1+**	**-4.10**
E114F00h~E115F00h	**191**	**Positive**	**190.97868**	**13086**	**190.97883**	**C5H4N4S**	**6-Mercaptopurin**	**[M+K]1+**	**-0.77**
			191.03095	**1121**	**191.03163**	**C5H12O5**	**Xylitol**	**[M+K]1+**	**-3.58**
			191.10584	**1280**	**191.10666**	**C12H14O2**	**Propyl cinnamate**	**[M+H]1+**	**-4.28**
2N=10~2N=20	**194.09**	**Positive**	193.98188	1153	193.98250	C2H6NO6P	Phosphoglycolo hydroxamate	[M+Na]1+	-3.19
			194.05861	**2340**	**194.05779**	**C8H13NO2**	**Scopoline**	**[M+K]1+**	**4.24**
E114F00h~E480F00h	**195.09**	**Positive**	**194.94495**	**1000**	**194.94554**	**C2H5O6P**	**2-Phospho glycolate**	**[M+K]1+**	**-3.01**
			195.04121	**1120**	**195.04180**	**C8H12O3**	**5-Oxo-7-octenoate**	**[M+K]1+**	**-3.04**
			195.07739	**1148**	**195.07819**	**C9H16O2**	**2-Nonenoate**	**[M+K]1+**	**-4.10**
			195.08573	**1539**	**195.08632**	**C7H14O6**	**Methyl glucoside**	**[M+H]1+**	**-3.01**
			195.09854	**1007**	**195.09917**	**C9H16O3**	**3-Caproyl propionate**	**[M+Na]1+**	**-3.21**
2N=10~2N=20	203.18	Positive	203.05182	2016	203.05261	C6H12O6	Glucose	[M+Na]1+	-3.90
2N=10~2N=30	**208.09**	**Positive**	207.99759	1383	207.99815	C3H8NO6P	*O*-Phospho serine	[M+Na]1+	-2.68
			208.04799	**2098**	**208.04829**	**C7H11N3O2**	**1- or 3-Methyl histidine**	**[M+K]1+**	**-1.42**
E160F00h~E260F00h	**210**	**Positive**	**209.95588**	**9407**	**209.95644**	**C2H6NO6P**	**Phosphoglycolo hydroxamate**	**[M+K]1+**	**-2.64**
			210.05198	**1232**	**210.05255**	**C11H9NO2**	**Indole acrylate**	**[M+Na]1+**	**-2.71**
2N=10~2N=30	**211.09**	**Positive**	**210.93987**	**26857**	**-**	**-**	**Unknown**	**-**	**-**
			211.03597	**1135**	**211.03672**	**C8H12O4**	**4-Octenedioate**	**[M+K]1+**	**-3.55**
			211.04879	**1421**	**211.04795**	**C7H12N2O3**	**Glycyl proline**	**[M+K]1+**	**3.97**
			211.07240	**3275**	**211.07310**	**C9H16O3**	**6-Propionyl N-caproate**	**[M+K]1+**	**-3.34**
			211.09351	612	211.09408	C9H16O4	Azelaic acid	[M+Na]1+	-2.70
			211.13208	802	211.13287	C12H18O3	Jasmonate	[M+H]1+	-3.75
E114F00h~E160F00h	**214.09**	**Positive**	**214.04679**	**1746**	**214.04747**	**C10H9NO3**	**Indole-3-glycolate**	**[M+Na]1+**	**-3.15**
			214.05817	**49449**	**214.05885**	**C6H13N3O3**	**Citrulline**	**[M+K]1+**	**-3.18**
E129F00h~E137F00h	**215**	**Positive**	**215.01556**	**8683**	**215.01623**	**C6H8O7**	**2-Keto-3-deoxy glucarate**	**[M+Na]1+**	**-3.10**
			215.03094	**1850**	**215.03163**	**C7H12O5**	**2-Isopropyl malate**	**[M+K]1+**	**-3.22**
			215.05057	**1744**	**215.05026**	**C8H16O2S**	**6-Thio-octanoate**	**[M+K]1+**	**1.43**
E129F00h~E480F00h	**217.18**	**Positive**	**217.01024**	**5010**	**217.01079**	**C4H9O8P**	**Erythronate-4-phosphate**	**[M+H]1+**	**-2.51**

			217.03135	10870	217.03188	C6H10O7	Glucuronate	[M+Na]1+	-2.42
E115F00h~E480F00h	219.09	Positive	219.02584	46171	219.02655	C6H12O6	Glucose	[M+K]1+	-3.23
E137F00h~E176F00h	224.09	Positive	223.97144	18021	223.97209	C3H8NO6P	Phospho serine	[M+K]1+	-2.88
			224.07594	22054	224.07648	C7H10O7	Homocitrate	[M+NH4]1+	-2.41
E176F00h~E480F00h	225	Positive	224.95539	1040	224.95610	C3H7O7P	3-Phospho glycerate	[M+K]1+	-3.16
			225.05162	2070	225.05237	C9H14O4	2-Carboxy cyclohexyl acetate	[M+K]1+	-3.33
			225.06340	1093	225.06345	C11H10N2O2	Didehydro tryptophan	[M+Na]1+	-0.22
			225.07447	2789	225.07335	C9H14O5	Diethyl 2-methyl-3-oxosuccinate	[M+Na]1+	4.99
			225.08794	1523	225.08699	C10H12N2O4	3-Hydroxy kynurenine	[M+H]1+	4.24
			225.09912	1113	225.09849	C10H12N5	N6-Dimethyl allyl adenine	[M+Na]1+	2.79
			225.14784	1650	225.14852	C13H20O3	Vomifoliol	[M+H]1+	-3.03
E115F00h~E137F00h	227.09	Positive	226.99449	837	226.99525	C7H8O6	Homoaconitate	[M+K]1+	-3.34
			227.01534	2207	227.01623	C7H8O7	Oxaloglutarate	[M+Na]1+	-3.90
			227.03089	1265	227.03163	C8H12O5	2-Oxo suberate	[M+K]1+	-3.27
			227.04211	901	227.04287	C7H12N2O4	N-Acetyl glutamine	[M+K]1+	-3.33
			227.06706	1584	227.06802	C9H16O4	Azelaic acid	[M+K]1+	-4.22
			227.07882	1519	227.07910	C11H12N2O2	Tryptophan	[M+Na]1+	-1.23
E114F00h~E480F00h	229.18	Positive	229.03122	984	229.03188	C7H10O7	Homocitrate	[M+Na]1+	-2.86
			229.04637	1270	229.04717	C6H13O7P	Mevalonate-5P	[M+H]1+	-3.49
			229.05803	1061	229.05852	C7H14N2O4	Diamino pimelate	[M+K]1+	-2.12
			229.14253	1935	229.14344	C12H20O4	Traumatate	[M+H]1+	-3.96
2N=10~2N=30	231.09	Positive	230.98947	75153	230.99016	C6H8O7	2,5-Didehydro gluconate	[M+K]1+	-3.00
			231.02564	5353	231.02655	C7H12O6	Quinate	[M+K]1+	-3.93
			231.06335	1208	231.06278	C11H12O4	Sinapaldehyde	[M+Na]1+	2.46
			231.09853	808	231.09755	C9H14N2O5	Aspartyl proline	[M+H]1+	4.24
			231.13499	877	231.13394	C5H9NO2	Proline	[2M+H]1+	4.56
2N=10~2N=20	233.18	Positive	232.98746	3254	-	-	41K Isotope of 2,5-Didehydro gluconate	[M+K]1+	-
			233.00481	978	233.00581	C6H10O7	Glucuronate	[M+K]1+	-4.30
			233.04129	1727	233.04205	C10H10O5	2-Hydroxy ferulate	[M+Na]1+	-3.24
			233.07766	1432	233.07843	C11H14O4	Sinapyl Alcohol	[M+Na]1+	-3.31
2N=20~2N=30	235.09	Positive	235.02053	2221	235.02146	C6H12O7	Gluconate	[M+K]1+	-3.97
			235.07232	13897	235.07295	C14H12O2	4,4'-Dihydroxy stilbene	[M+Na]1+	-2.68
			235.16433	32627	235.16524	C5H11NO2	Valine	[2M+H]1+	-3.85

E137F00h~E162F00h	**236.09**	**Positive**	**236.03254**	**1383**	**236.03197**	**C9H11NO4**	**DOPA**	**[M+K]1+**	**2.42**
			236.04339	**1387**	**236.04320**	**C8H11N3O3**	**Acetyl histidine**	**[M+K]1+**	**0.80**
			236.07573	**1054**	**236.07648**	**C8H13NO7**	**N-Acetyl galactosaminate**	**[M+H]1+**	**-3.18**
2N=20~2N=30	**237.09**	**Positive**	**237.05138**	**1440**	**237.05222**	**C13H10O3**	**Phenyl salicylate**	**[M+Na]1+**	**-3.53**
			237.08795	**4236**	**237.08699**	**C11H12N2O4**	**N-Formyl kynurenine**	**[M+H]1+**	**4.07**
			237.14798	**1584**	**237.14852**	**C14H20O3**	**4-Heptyl oxybenzoate**	**[M+H]1+**	**-2.29**
2N=10~2N=20	**241**	**Positive**	**240.86532**	**135571**	**-**	**-**	**Unknown**	**-**	**-**
			241.04647	**1367**	**241.04728**	**C9H14O5**	**Diethyl-2-methyl-3-oxosuccinate**	**[M+K]1+**	**-3.37**
			241.08285	**1779**	**241.08367**	**C10H18O4**	**Sebacate**	**[M+K]1+**	**-3.39**
			241.09412	**7711**	**241.09475**	**C12H14N2O2**	**Acetyl serotonin**	**[M+Na]1+**	**-2.61**
			241.15383	**1693**	**241.15467**	**C12H20N2O3**	**Slaframine**	**[M+H]1+**	**-3.48**
2N=20~2N=30	**241.72**	**Positive**	**241.58886**	**1724**	**241.58844**	**C21H31N3O5S**	**FMLP**	**[M+2Na]2+**	**1.72**
2N=10~2N=20	**243**	**Positive**	242.98919	7016	242.99016	C7H8O7	Oxaloglutarate	[M+K]1+	-4.00
			243.01001	**1324**	**243.01114**	**C7H8O8**	**4-Oxalo citramalate**	**[M+Na]1+**	**-4.65**
			243.04499	688	-	-	41K Isotope of Diethyl-2-methyl-3-oxosuccinate	[M+K]1+	-
			243.05196	1314	243.05304	C11H12N2O2	Tryptophan	[M+K]1+	-4.43
2N=20~2N=30	**244.18**	**Positive**	**244.02103**	**1183**	**244.02165**	**C10H7NO5**	**7,8-Dihydroxy kynurenate**	**[M+Na]1+**	**-2.52**
			244.05712	**1063**	**244.05818**	**C8H15NO5**	**N-Acetyl-fucosamine**	**[M+K]1+**	**-4.35**
			244.09365	**2547**	**244.09457**	**C9H19NO4**	**Pantothenol**	**[M+K]1+**	**-3.76**
2N=10~2N=30	**245.09**	**Positive**	244.98731	908	-	-	41K Isotope of Oxaloglutarate	[M+K]1+	-
			245.00482	**22984**	**245.00581**	**C7H10O7**	**Homocitrate**	**[M+K]1+**	**-4.05**
2N=10~2N=30	**246.09**	**Positive**	**246.02763**	**1156**	**246.02755**	**C9H9N3O3**	**Methyl 5-hydroxy-2-benzimidazole carbamate**	**[M+K]1+**	**0.33**
E160F00h~E176F00h	**249.09**	**Positive**	**249.03617**	**3231**	**249.03696**	**C10H10O6**	**Chorismate**	**[M+Na]1+**	**-3.18**
			249.08800	**1382**	**249.08875**	**C12H18O3**	**Jasmonate**	**[M+K]1+**	**-3.02**
E137F00h~E160F00h	**251.09**	**Positive**	**251.06733**	**1327**	**251.06787**	**C14H12O3**	**Resveratrol**	**[M+Na]1+**	**-2.13**
			251.09430	**1157**	**251.09451**	**C14H16N2**	**3,3'-Dimethyl benzidine**	**[M+K]1+**	**-0.82**
			251.10356	**4929**	**251.10440**	**C12H20O3**	**12-Oxo-10-dodecenoate**	**[M+K]1+**	**-3.36**
			251.14027	**1008**	**251.13902**	**C13H18N2O3**	**N-Caffeoyl putrescine**	**[M+H]1+**	**4.98**
2N=10~2N=30	**255.18**	**Positive**	**255.02727**	**763**	**255.02644**	**C7H11O8P**	**Shikimate-3-phosphate**	**[M+H]1+**	**3.27**
			255.08606	**1175**	**255.08540**	**C8H16N4O3**	**N-α-Acetyl arginine**	**[M+K]1+**	**2.59**
			255.09846	**1538**	**255.09932**	**C11H20O4**	**Undecane dioate**	**[M+K]1+**	**-3.37**
			255.10672	**909**	**255.10745**	**C9H18O8**	**Galactosyl glycerol**	**[M+H]1+**	**-2.85**
			255.13509	**1251**	**255.13570**	**C12H24O3**	**α-Hydroxy laurate**	**[M+K]1+**	**-2.41**

2N=20~2N=30	**257.08**	**Positive**	**257.05297**	**1020**	**257.05343**	**C8H14N2O5**	**γ-Glutamyl alanine**	**[M+K]1+**	**-1.79**
			257.07753	**1959**	**257.07858**	**C10H18O5**	**3-Hydroxy sebacate**	**[M+K]1+**	**-4.10**
			257.14639	3440	257.14718	C5H11NO2	Valine	[2M+Na]1+	-3.07
E162F00h~E176F00h	**258.18**	**Positive**	**258.07327**	**1410**	**258.07383**	**C9H17NO5**	**Pantothenate**	**[M+K]1+**	**-2.18**
2N=10~2N=30	**259**	**Positive**	**259.02067**	**3169**	**259.02146**	**C8H12O7**	**(Homo)2-citrate**	**[M+K]1+**	**-3.06**
			259.05729	**1131**	**259.05770**	**C12H12O5**	**5,6,7-Trimethoxy coumarin**	**[M+Na]1+**	**-1.57**
			259.12920	**1059**	**259.13047**	**C14H20O3**	**Heptyl *p*-hydroxybenzoate**	**[M+Na]1+**	**-4.89**
E114F00h~E480F00h	**261.18**	**Positive**	261.01874	1463	-	-	41K Isotope of (Homo)2-citrate	[M+K]1+	-
			261.03641	1046	261.03700	C6H13O9P	Glucose 6-phosphate	[M+H]1+	-2.26
			261.05143	**9757**	**261.05237**	**C12H14O4**	**Coniferyl acetate**	**[M+K]1+**	**-3.60**
			261.07256	**1453**	**261.07335**	**C12H14O5**	**3,4,5-Trimethoxy cinnamate**	**[M+Na]1+**	**-3.01**
			261.08803	**1824**	**261.08875**	**C13H18O3**	**Dehydro vomifoliol**	**[M+K]1+**	**-2.77**
E333F00h~E480F00h	**263.08**	**Positive**	263.04952	2127	-	-	41K Isotope of Coniferyl acetate	[M+K]1+	-
			263.10365	**18497**	**263.10440**	**C13H20O3**	**Vomifoliol**	**[M+K]1+**	**-2.86**
E137F00h~E162F00h	264.18	Positive	264.10693	2008	-	-	13C Isotope of Vomifoliol	[M+K]1+	-
2N=20~2N=30	**268.18**	**Positive**	**268.10297**	**10555**	**268.10403**	**C10H13N5O4**	**Adenosine**	**[M+H]1+**	**-3.96**
			268.13880	**1059**	**268.13801**	**C9H19N5O3**	**β-Alanyl arginine**	**[M+Na]1+**	**2.94**
E129F00h~E137F00h	**269.18**	**Positive**	**268.98160**	**3680**	**268.98232**	**C5H11O8P**	**Ribose-5-phosphate**	**[M+K]1+**	**-2.67**
			269.08883	899	269.08982	C5H9NO2	Proline	[2M+K]1+	-3.66
			269.09649	**1194**	**269.09609**	**C20H12O**	**2-Hydroxybenzo[α]pyrene**	**[M+H]1+**	**1.48**
			269.11413	**1568**	**269.11497**	**C12H22O4**	**Diisopropyl adipate**	**[M+K]1+**	**-3.11**
2N=10~2N=30	**271.08**	**Positive**	**271.07624**	**1348**	**271.07648**	**C11H20O3S**	**2-Oxo-10-methyl thiodecanoate**	**[M+K]1+**	**-0.88**
			271.08316	**1012**	**271.08434**	**C13H16N2O2**	**Melatonin**	**[M+K]1+**	**-4.34**
			271.09335	**1554**	**271.09408**	**C14H16O4**	**Prenyl caffeate**	**[M+Na]1+**	**-2.70**
E114F00h~E176F00h	273.18	Positive	273.12024	46230	273.12112	C5H11NO2	Valine	[2M+K]1+	-3.21
E162F00h~E333F00h	**275.08**	**Positive**	**275.01541**	**11332**	**275.01627**	**C6H11O10P**	**Glucuronate 1-phosphate**	**[M+H]1+**	**-3.11**
			275.10345	1355	275.10264	C7H7NO2	*p*-Amino benzoate	[2M+H]1+	2.96
			275.11842	2918	-	-	41K Isotope of Valine	[2M+K]1+	-
E129F00h~E137F00h	**277.18**	**Positive**	**277.03127**	**71614**	**277.03203**	**C8H14O8**	**3-Deoxy octulosonate**	**[M+K]1+**	**-2.74**
			277.11937	**4202**	**277.12005**	**C14H22O3**	**1α,1β-Dihomo jasmonate**	**[M+K]1+**	**-2.46**
			277.14024	**1156**	**277.13942**	**C11H20N2O6**	**Saccharopine**	**[M+H]1+**	**2.98**
E129F00h~E137F00h	278.18	Positive	278.03456	3855	-	-	13C Isotope of 3-Deoxy octulosonate	[M+K]1+	-
E129F00h~E137F00h	**279.18**	**Positive**	279.02923	2862	-	-	41K Isotope of 3-Deoxy octulosonate	[M+K]1+	-

			279.04695	3228	279.04768	C4H8O4	Erythrose	[2M+K]1+	-2.61
			279.05510	**12070**	**-**	**-**	**Unknown**	**-**	**-**
			279.09858	**5363**	**279.09917**	**C16H16O3**	**Pterostilbene**	**[M+Na]1+**	**-2.10**
			279.11039	1143	279.11055	C12H20N2O3	Slaframine	[M+K]1+	-0.58
2N=10~2N=20	**282.18**	**Positive**	**282.11119**	**938**	**282.11022**	**C12H21NO4**	**Tiglyl carnitine**	**[M+K]1+**	**3.45**
			282.14585	**8763**	**282.14483**	**C13H19N3O4**	**Pendimethalin**	**[M+H]1+**	**3.60**
			282.27856	935	282.27914	C18H35NO	Oleamide	[M+H]1+	-2.06
E129F00h~E480F00h	**283.18**	**Positive**	283.01969	988	283.01894	C6H13O9P	Glucose 6-phosphate	[M+Na]1+	2.64
			283.12986	**1123**	**283.13062**	**C13H24O4**	**2-Methyl-dodecanedioate**	**[M+K]1+**	**-2.68**
			283.26204	**1007**	**283.26316**	**C18H34O2**	**Oleate**	**[M+H]1+**	**-3.94**
E115F00h~E129F00h	286.08	Positive	286.07658	881	286.07688	C4H6O5	Malate	[2M+NH4]1+	-1.03
			286.11236	899	286.11326	C9H16O9	Glucosyl glycerate	[M+NH4]1+	-3.15
2N=10~2N=30	**287.18**	**Positive**	**286.96626**	**1239**	**286.96648**	**C3H8OS2**	**6-Acetyl dihydrolipoate**	**[2M+K]1+**	**-0.78**
			287.00047	**1502**	**287.00097**	**C4H4O5**	**Oxaloacetate**	**[2M+Na]1+**	**-1.75**
			287.14064	**1344**	**287.14079**	**C16H24O2**	**8,10-Hexadeca diynoate**	**[M+K]1+**	**-0.52**
			287.16106	**4540**	**287.16177**	**C16H24O3**	**Dehydro juvabione**	**[M+Na]1+**	**-2.46**
E162F00h~E485F00h	**294.18**	**Positive**	**294.06596**	**1051**	**-**	**-**	**Unknown**	**-**	**-**
			294.07304	**992**	**294.07368**	**C15H13NO4**	**Benzoyl-4-methoxy anthranilate**	**[M+Na]1+**	**-2.18**
			294.11756	**1187**	**294.11835**	**C11H19NO8**	**N-Acetyl muramate**	**[M+H]1+**	**-2.67**
E333F00h~E480F00h	**295.18**	**Positive**	**295.11245**	**1651**	**295.11360**	**C5H9NO4**	**Glutamate**	**[2M+H]1+**	**-3.88**
			295.12957	**2824**	**295.12885**	**C14H18N2O5**	**Glutamyl phenylalanine**	**[M+H]1+**	**2.44**
2N=10~2N=20	**296.18**	**Positive**	**296.06510**	**14680**	**296.06599**	**C8H20NO6P**	**Glycero phosphocholine**	**[M+K]1+**	**-2.99**
			296.12753	**1655**	**296.12812**	**C18H17NO3**	**Xylopine**	**[M+H]1+**	**-2.00**
E114F00h~E160F00h	**299.18**	**Positive**	298.99236	786	298.99288	C6H13O9P	Glucose 6-phosphate	[M+K]1+	-1.75
			299.08852	**1486**	**299.08915**	**C6H10O3**	**2-Keto-N-caproate**	**[2M+K]1+**	**-2.10**
2N=10~2N=20	**303.18**	**Positive**	**303.00705**	**1119**	**303.06631**	**C11H20O5S**	**2-(6'-Methylthio)hexylmalate**	**[M+K]1+**	**-195.52**
			303.08325	**20028**	**-**	**-**	**Unknown**	**-**	**-**
			303.09842	**1223**	**303.09932**	**C15H20O4**	**Abscisate**	**[M+K]1+**	**-2.96**
2N=10~2N=30	**307.18**	**Positive**	307.04192	967	307.04259	C9H16O9	Glucosyl glycerate	[M+K]1+	-2.20
			307.07813	**1430**	**307.07898**	**C5H10O4**	**Deoxy ribose**	**[2M+K]1+**	**-2.76**
			307.09341	**1005**	**307.09408**	**C17H16O4**	**Phenethyl caffeate**	**[M+Na]1+**	**-2.18**
			307.20234	**1025**	**307.20339**	**C17H32O2**	**3-Hepta decenoate**	**[M+K]1+**	**-3.41**
2N=10~2N=20	**312.08**	**Positive**	**311.89147**	**4346**	**-**	**-**	**Unknown**	**-**	**-**

			312.22905	**893**	**312.22994**	**C16H35NO2**	**C16 Sphinganine**	**[M+K]1+**	**-2.84**
E137F00h~E480F00h	**313.18**	**Positive**	313.02811	1026	313.02951	C7H15O10P	Sedoheptulose 7-phosphate	[M+Na]1+	-4.47
			313.09405	**4456**	**313.09490**	**C15H18N2O3**	**Indole-3-acetyl-valine**	**[M+K]1+**	**-2.72**
			313.11525	**3049**	**313.11588**	**C15H18N2O4**	**6-Hydroxy-indole-3-acetyl-valine**	**[M+Na]1+**	**-2.01**
			313.15545	**2614**	**313.15644**	**C18H26O2**	**17-Octadecene-9,11-Diynoate**	**[M+K]1+**	**-3.15**
E129F00h~E162F00h	**314**	**Positive**	**314.12283**	**1118**	**314.12343**	**C14H19NO7**	**Tyramine glucuronide**	**[M+H]1+**	**-1.91**
			314.15923	1439	314.15982	C15H20O6	Vomitoxin	[M+NH4]1+	-1.87
E129F00h~E160F00h	**315**	**Positive**	**314.98717**	**1328**	**314.98780**	**C6H13O10P**	**6-Phospho gluconate**	**[M+K]1+**	**-1.99**
			315.08290	**1015**	**315.08391**	**C15H16O6**	**Dihydro mikanolide**	**[M+Na]1+**	**-3.21**
			315.13468	**1242**	**315.13570**	**C17H24O3**	**[6]-Shogaol**	**[M+K]1+**	**-3.25**
E176F00h~E484F00h	**316.18**	**Positive**	**316.16621**	**763**	**316.16734**	**C17H27NO2**	**Venlafaxine**	**[M+K]1+**	**-3.56**
			316.21053	**725**	**316.21185**	**C16H29NO5**	**Butoctamide hydrogen succinate**	**[M+H]1+**	**-4.18**
E333F00h~E480F00h	**319.18**	**Positive**	**319.09611**	**1010**	**319.09649**	**C20H14O4**	**8-O-Methyl tetrangulol**	**[M+H]1+**	**-1.18**
			319.11456	**3308**	**319.11521**	**C15H20O6**	**Vomitoxin**	**[M+Na]1+**	**-2.04**
			319.12972	**1300**	**319.13047**	**C19H20O3**	**4-Prenyl resveratrol**	**[M+Na]1+**	**-2.34**
E114F00h~E176F00h	**320.18**	**Positive**	**320.04634**	**1171**	**320.04658**	**C12H15N3O3S**	**Albendazole oxide**	**[M+K]1+**	**-0.73**
			320.11783	**1115**	**320.11935**	**C14H23N3OS**	**Xanomeline**	**[M+K]1+**	**-4.73**
			320.23404	**2395**	**320.23502**	**C18H35NO**	**Oleamide**	**[M+K]1+**	**-3.07**
E129F00h~E137F00h	**323.18**	**Positive**	**322.98018**	**841**	**322.98087**	**C6H6O2S**	**Thien-2-ylacetate**	**[2M+K]1+**	**-2.12**
			323.07295	**1418**	**323.07374**	**C13H16O8**	**4-(β-Glucosyloxy)benzoate**	**[M+Na]1+**	**-2.45**
			323.08833	**1189**	**323.08738**	**C14H14N2O7**	**3-Hydroxy-2-oxindole-3-acetyl-aspartate**	**[M+H]1+**	**2.94**
			323.12456	**1345**	**323.12538**	**C18H20O4**	**Toxyl angelate**	**[M+Na]1+**	**-2.54**
			323.14496	628	323.14490	C6H11NO4	2-Amino adipate	[2M+H]1+	0.20
E114F00h~E137F00h	**326**	**Positive**	**326.10752**	**561**	**326.10818**	**C11H19NO10**	**N-Glycolyl neuraminate**	**[M+H]1+**	**-2.01**
			326.14338	**1652**	**-**	**-**	**Unknown**	**-**	**-**
			326.17998	**1695**	**326.17845**	**C17H27NO3S**	**Cycloxydim**	**[M+H]1+**	**4.71**
2N=10~2N=30	**329.18**	**Positive**	329.00396	571	329.00345	C7H15O10P	Sedoheptulose 7-phosphate	[M+K]1+	1.56
			329.13524	**1005**	**329.13595**	**C17H22O5**	**Xanthinin**	**[M+Na]1+**	**-2.15**
			329.15046	**5330**	**329.15135**	**C18H26O3**	**8-Oxo-9,11-octadecadiynoate**	**[M+K]1+**	**-2.72**
			329.17147	**600**	**329.17233**	**C18H26O4**	**Di-N-Pentyl phthalate**	**[M+Na]1+**	**-2.62**
2N=10~2N=20	**341.9**	**Positive**	**341.81673**	**41617**	**-**	**-**	**Unknown**	**-**	**-**
			342.13892	**1295**	**342.13948**	**C12H23NO10**	**6-(α-Glucosaminyl)-1myo-inositol**	**[M+H]1+**	**-1.63**
E176F00h~E480F00h	**343.18**	**Positive**	**343.07810**	**4656**	**343.07883**	**C16H16O7**	***p*-Coumaroyl shikimate**	**[M+Na]1+**	**-2.12**

			343.11495	**1552**	**343.11360**	**C7H9NO4**	**5-Deoxy-5-amino-3-dehydroshikimate**	**[2M+H]1+**	**3.95**
			343.12417	590	343.12349	C12H22O11	Sucrose	[M+H]1+	1.98
E114F00h~E480F00h	**345.18**	**Positive**	**345.09400**	**15428**	**-**	**-**	**Unknown**	**-**	**-**
			345.11969	**1719**	**345.12096**	**C19H18N2O3**	***p*-Coumaroyl serotonin**	**[M+Na]1+**	**-3.69**
			345.14563	**2180**	**345.14627**	**C18H26O4**	**Dipentyl phthalate**	**[M+K]1+**	**-1.85**
E114F00h~E333F00h	**351.18**	**Positive**	351.04685	2791	351.04653	C6H16N4O9P2	N-Phospho lombricine	[M+H]1+	0.90
			351.06790	**1956**	**351.06881**	**C11H20O10**	**Arabino galactose**	**[M+K]1+**	**-2.59**
			351.08314	**1249**	**351.08406**	**C15H20O7**	**4-Hydroxycinnamyl alcohol 4-glucoside**	**[M+K]1+**	**-2.63**
			351.22849	**1113**	**351.22960**	**C19H36O3**	**10-Oxo-nonadecanoate**	**[M+K]1+**	**-3.17**
2N=10~2N=20	355.18	Positive	355.07808	3747	355.07898	C7H10O4	2-Isopropyl maleate	[2M+K]1+	-2.53
E114F00h~E480F00h	**357.27**	**Positive**	**357.09376**	**2291**	**357.09448**	**C17H18O7**	**Byakangelicin**	**[M+Na]1+**	**-2.01**
			357.11968	799	357.11801	C16H20O9	1-O-Feruloyl-β-glucose	[M+H]1+	4.67
			357.16688	**1099**	**357.16740**	**C16H30O6**	**Menthyl O-β-Glucoside**	**[M+K]1+**	**-1.45**
2N=10~2N=20	**359.18**	**Positive**	**358.99200**	**6133**	**358.99376**	**C12H17O4PS2**	**Phenthoate**	**[M+K]1+**	**-4.89**
			359.09880	**853**	**359.10027**	**C14H19N2O7P**	**α-Ribazole-5'-P**	**[M+H]1+**	**-4.09**
			359.10943	**5379**	**359.11028**	**C14H24O8**	**Valproate glucuronide**	**[M+K]1+**	**-2.36**
			359.12428	**757**	**359.12377**	**C9H9NO3**	**Hippurate**	**[2M+H]1+**	**1.43**
			359.14595	**1388**	**359.14623**	**C16H18N6O4**	**2-Phenyl amino adenosine**	**[M+H]1+**	**-0.78**
2N=20~2N=30	**364.09**	**Positive**	**364.12285**	**1440**	**364.12142**	**C12H23NO10**	**Lactosamine**	**[M+Na]1+**	**3.93**
			364.26016	**977**	**364.26124**	**C20H39NO2**	**N-Oleoyl ethanolamine**	**[M+K]1+**	**-2.96**
E114F00h~E162F00h	365.27	Positive	365.10457	21308	365.10544	C12H22O11	Sucrose	[M+Na]1+	-2.37
E114F00h~E162F00h	366.27	Positive	366.10794	2246	-	-	13C Isotope of Sucrose	[M+Na]1+	-
E162F00h~E333F00h	**367.18**	**Positive**	366.96049	2007	366.95933	C7H15O10P	Sedoheptulose 7-phosphate	[M+2K-H]1+	3.17
			367.11496	**995**	**367.11536**	**C16H24O7**	**Prostaglandin M**	**[M+K]1+**	**-1.10**
			367.18736	**2032**	**367.18813**	**C18H32O5**	**9,10,11-Trihydroxy-12,15-octadecadienoate**	**[M+K]1+**	**-2.11**
			367.22398	**1011**	**367.22437**	**C22H32O3**	**7-Hydroxy-4Z,8E,10Z,13Z,16Z,19Z-docosahexenoic acid**	**[M+Na]1+**	**-1.05**
E114F00h~E480F00h	**371.27**	**Positive**	**371.10953**	**10921**	**-**	**-**	**Unknown**	**-**	**-**
			371.14634	**2118**	**371.14651**	**C19H24O6**	**Gibberellin A34**	**[M+Na]1+**	**-0.46**
E114F00h~E480F00h	**373.27**	**Positive**	**373.01876**	**1381**	**373.01977**	**C11H15N2O8P**	**Nicotinamide ribotide**	**[M+K]1+**	**-2.69**
			373.02897	**900**	**373.02966**	**C9H19O11P**	**2-(Glucosyl)-sn-glycerol 3-phosphate**	**[M+K]1+**	**-1.85**
			373.12536	**66710**	**-**	**-**	**Unknown**	**-**	**-**
			373.15042	**861**	**373.14931**	**C17H24O9**	**Syringin**	**[M+H]1+**	**2.97**
			373.17715	**2272**	**373.17757**	**C20H30O4**	**PGA2**	**[M+K]1+**	**-1.12**

E129F00h~E480F00h	**374.18**	**Positive**	374.12897	6759	-	-	13C Isotope of 373.12536	-	-
			374.28115	**1397**	**-**	**-**	**Unknown**	**-**	**-**
E114F00h~E480F00h	**375.18**	**Positive**	**375.12268**	**3266**	**375.12367**	**C18H24O5S**	**Estradiol-17β 3-sulfate**	**[M+Na]1+**	**-2.64**
			375.13106	**5819**	**375.13153**	**C20H20N2O4**	**Feruloyl serotonin**	**[M+Na]1+**	**-1.25**
			375.19291	**1155**	**375.19322**	**C20H32O4**	**8,15-Dihydroxy-5,9,11,13-eicosatetraenoate**	**[M+K]1+**	**-0.82**
E129F00h~E137F00h	377.27	Positive	377.06240	1217	377.06333	C16H18O8	*p*-Coumaroyl quinate	[M+K]1+	-2.46
			377.07047	1148	377.07146	C7H8O6	Homoaconitate	[2M+H]1+	-2.62
E114F00h~E137F00h	**381.18**	**Positive**	**381.07882**	**821755**	**381.07937**	**C12H22O11**	**Sucrose**	**[M+K]1+**	**-1.45**
E114F00h~E137F00h	382.18	Positive	382.08183	75346	-	-	13C Isotope of Sucrose	[M+K]1+	-
E114F00h~E137F00h	383.18	Positive	383.07674	35850	-	-	41K Isotope of Sucrose	[M+K]1+	-
2N=20~2N=30	**384.18**	**Positive**	384.08042	3380	-	-	41K Isotope of 13C isotope of Sucrose	[M+K]1+	-
			384.14973	**664**	**384.15004**	**C14H25NO11**	**N-Acetyl lactosamine**	**[M+H]1+**	**-0.81**
			384.29526	**1198**	**-**	**-**	**Unknown**	**-**	**-**
E129F00h~E480F00h	**385.18**	**Positive**	**385.09929**	**1026**	**385.10078**	**C7H11NO4**	**5-Deoxy-5-aminoshikimate**	**[2M+K]1+**	**-3.86**
			385.11394	**771**	**385.11293**	**C17H20O10**	**O-Sinapoyl glucarolactone**	**[M+H]1+**	**2.63**
			385.12525	**4188**	**385.12578**	**C19H22O7**	**Vernolide**	**[M+Na]1+**	**-1.37**
			385.16174	**1610**	**385.16231**	**C17H30O7**	**3-Hydroxytetradecane-1,3,4-tricarboxylate**	**[M+K]1+**	**-1.49**
			385.19862	**1031**	**385.19870**	**C18H34O6**	**9,10-Dihydroxy octadecanedioate**	**[M+K]1+**	**-0.20**
E114F00h~E480F00h	**387.27**	**Positive**	387.10467	8699	387.10504	C9H10O4	Dihydro caffeate	[2M+Na]1+	-0.96
			387.14070	**10059**	**387.14158**	**C8H14O4**	**Suberate**	**[2M+K]1+**	**-2.27**
			387.17738	**1390**	**387.17781**	**C20H28O6**	**Gibberellin A37**	**[M+Na]1+**	**-1.11**
			387.19307	**837**	**387.19322**	**C21H32O4**	**17α,21-Dihydroxy pregnenolone**	**[M+K]1+**	**-0.38**
E137F00h~E480F00h	**389.18**	**Positive**	**389.00301**	**2661**	**389.00242**	**C6H16N4O9P2**	**N-Phospho lombricine**	**[M+K]1+**	**1.53**
			389.08377	**1109**	**389.08196**	**C18H22O5S**	**Estrone 3-sulfate**	**[M+K]1+**	**4.66**
			389.09439	1944	389.09259	C6H10O7	Glucuronate	[2M+H]1+	4.63
			389.10347	959	389.10229	C5H13NO4S	Choline sulfate	[2M+Na]1+	3.04
			389.12027	**18046**	**389.12156**	**C19H26O3S2**	**1α,5α-Epidithio-17a-oxahomoandrostan-3,17-dione**	**[M+Na]1+**	**-3.33**
			389.14693	**5337**	**389.14556**	**C9H10N2O3**	**4-Amino hippurate**	**[2M+H]1+**	**3.51**
			389.17178	**1901**	**389.17248**	**C20H30O5**	**PGD3**	**[M+K]1+**	**-1.81**
2N=10~2N=20	**391**	**Positive**	391.09958	1138	391.10011	C7H12O5	2-Isopropyl malate	[2M+K]1+	-1.35
			391.17189	**1055**	**391.17288**	**C8H16O4**	**6,8-Dihydroxy octanoate**	**[2M+K]1+**	**-2.53**
			391.18751	**1896**	**391.18813**	**C20H32O5**	**PGD2**	**[M+K]1+**	**-1.59**
			391.22398	**1441**	**391.22452**	**C21H36O4**	**Montanol**	**[M+K]1+**	**-1.38**

2N=10~2N=30	**392**	**Positive**	**392.15354**	**1213**	**392.15513**	**C16H25NO10**	**Proacaciberin**	**[M+H]1+**	**-4.04**
			392.29162	**15526**	**392.29254**	**C22H43NO2**	**Anandamide (20:L, N-9)**	**[M+K]1+**	**-2.34**
2N=10~2N=30	**393.27**	**Positive**	**393.20338**	**1003**	**393.20378**	**C20H34O5**	**PGD1**	**[M+K]1+**	**-1.02**
			393.23919	**1133**	**393.24006**	**C19H37O6P**	**PA(16:0/0:0)[Cyclic]**	**[M+H]1+**	**-2.20**
			393.27806	**1130**	**393.27655**	**C22H42O3**	**2-Oxo docosanoate**	**[M+K]1+**	**3.83**
E160F00h~E333F00h	**395.18**	**Positive**	**395.07328**	**4137**	**395.07389**	**C16H20O9**	**1-O-Feruloyl-β-glucose**	**[M+K]1+**	**-1.55**
E114F00h~E480F00h	**401.27**	**Positive**	**401.25738**	**1016**	**-**	**-**	**Unknown**	**-**	**-**
			401.26663	**1378**	**401.26623**	**C23H38O4**	**2-Arachidonoyl glycerol**	**[M+Na]1+**	**0.99**
E260F00h~E480F00h	**413.27**	**Positive**	**413.08344**	**1442**	**413.08446**	**C16H22O10**	**Secologanate**	**[M+K]1+**	**-2.46**
			413.09552	**1628**	**413.09433**	**C8H14O2S2**	**Lipoate**	**[2M+H]1+**	**2.87**
			413.12061	**1390**	**413.12084**	**C17H26O9**	**7-Deoxy loganin**	**[M+K]1+**	**-0.56**
			413.26581	**1433**	**413.26623**	**C24H38O4**	**Apocholate**	**[M+Na]1+**	**-1.02**
E129F00h~E480F00h	**415.27**	**Positive**	**415.09928**	**1494**	**415.10011**	**C16H24O10**	**Loganate**	**[M+K]1+**	**-1.99**
			415.13593	**9134**	**415.13634**	**C10H12O4**	**5-Hydroxy coniferyl alcohol**	**[2M+Na]1+**	**-0.99**
			415.17254	5231	415.17288	C9H16O4	Azelaic acid	[2M+K]1+	-0.82
			415.28170	**1296**	**415.28188**	**C24H40O4**	**Deoxy cholate**	**[M+Na]1+**	**-0.44**
E115F00h~E137F00h	**424.18**	**Positive**	**424.28177**	**34209**	**424.28222**	**C25H39NO3**	**Myxalamid B**	**[M+Na]1+**	**-1.05**
E129F00h~E160F00h	**425.27**	**Positive**	**425.08424**	**1629**	**425.08446**	**C17H22O10**	**1-O-Sinapoyl-β-glucose**	**[M+K]1+**	**-0.51**
			425.15663	**6915**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=20	**425.9**	**Positive**	**426.16041**	**1677**	**426.16061**	**C16H27NO12**	**Hyaluronate**	**[M+H]1+**	**-0.46**
			426.29810	**718**	**426.29790**	**C20H44NO6P**	**PC(O-12:0/0:0)[U]**	**[M+H]1+**	**0.46**
E114F00h~E480F00h	**431.27**	**Positive**	**431.16709**	**13562**	**431.16603**	**C9H13NO5**	**Succinyl proline**	**[2M+H]1+**	**2.47**
E114F00h~E480F00h	**432.27**	**Positive**	**432.13474**	**1150**	**-**	**-**	**Unknown**	**-**	**-**
			432.18749	**1222**	**432.18938**	**C23H27N3O4**	**Benexate hydrochloride**	**[M+Na]1+**	**-4.37**
2N=20~2N=30	**437.27**	**Positive**	**437.15684**	**1291**	**437.15708**	**C23H26O7**	**Neoisostegane**	**[M+Na]1+**	**-0.54**
			437.19329	**1586**	**437.19346**	**C24H30O6**	**Estra-1,3,5(10)-triene-3,6,17-triol triacetate**	**[M+Na]1+**	**-0.39**
			437.21040	**1079**	**437.20887**	**C25H34O4**	**Pregna-5,16,20-triene-3β,20-diol diacetate**	**[M+K]1+**	**3.50**
2N=10~2N=20	**441.27**	**Positive**	**441.15187**	**2003**	**441.15199**	**C22H26O8**	**Syring aresinol**	**[M+Na]1+**	**-0.27**
			441.33386	**1172**	**441.33392**	**C27H46O3**	**7α,25-Dihydroxy cholesterol**	**[M+Na]1+**	**-0.13**
2N=10~2N=20	**442.9**	**Positive**	443.07269	1195	443.07213	C10H7NO5	7,8-Dihydroxy kynurenate	[2M+H]1+	1.28
			443.20371	**1203**	**443.20407**	**C18H35O10P**	**PG(6:0/6:0)**	**[M+H]1+**	**-0.80**
			443.21909	**1070**	**443.21943**	**C24H36O5**	**12-Hydroxy-3,6-dioxo-5-cholan-24-oate**	**[M+K]1+**	**-0.77**
2N=20~2N=30	**445.27**	**Positive**	**445.11024**	**1027**	**445.11067**	**C17H26O11**	**Ipolamiide**	**[M+K]1+**	**-0.98**

			445.14681	**4940**	**445.14866**	**C15H28N2O11S**	**Desacetylmycothiol**	**[M+H]1+**	**-4.16**
			445.16403	**1441**	**445.16365**	**C23H26N4O3**	**Argentine**	**[M+K]1+**	**0.85**
			445.18312	**4901**	**445.18329**	**C22H30O8**	**Valtratum**	**[M+Na]1+**	**-0.38**
			445.23493	**1053**	**445.23508**	**C24H38O5**	**3-Oxo cholate**	**[M+K]1+**	**-0.34**
E333F00h~E480F00h	**449.18**	**Positive**	**449.10820**	**929**	**449.10784**	**C21H20O11**	**Kaempferol 7-O-glucoside**	**[M+H]1+**	**0.80**
			449.16789	1022	449.16669	C10H12N2O4	3-Hydroxy kynurenine	[2M+H]1+	2.66
E137F00h~E480F00h	451.18	Positive	451.04774	1462	451.04847	C7H10O7	Homocitrate	[2M+K]1+	-1.62
E114F00h~E115F00h	**455.18**	**Positive**	**455.09356**	**1776**	**455.09487**	**C21H20O10**	**Apigenin 7-O-β-glucoside**	**[M+Na]1+**	**-2.88**
			455.13104	**1957**	**455.13126**	**C22H24O9**	**Medicarpin-3-O-glucoside**	**[M+Na]1+**	**-0.47**
			455.16782	**1615**	**455.16602**	**C10H13NO5**	**L-Arogenate**	**[2M+H]1+**	**3.94**
E114F00h~E480F00h	**457.27**	**Positive**	**457.00882**	**1491**	**457.01098**	**C7H4N2O7**	**3,5-Dinitro salicylate**	**[2M+H]1+**	**-4.73**
			457.11049	**1328**	**457.11052**	**C21H22O10**	**Naringenin 7-O-β-glucoside**	**[M+Na]1+**	**-0.07**
			457.21019	**1515**	**457.21159**	**C21H39O6P**	**cPA(18:1(11Z)/0:0)**	**[M+K]1+**	**-3.06**
			457.23486	**1015**	**457.23332**	**C25H32N2O6**	**Vindoline**	**[M+H]1+**	**3.38**
2N=10~2N=30	**458.18**	**Positive**	**458.21318**	**1115**	**458.21465**	**C21H27N7O5**	**O-Demethyl puromycin**	**[M+H]1+**	**-3.20**
E333F00h~E480F00h	**459.27**	**Positive**	**459.06979**	**749**	**459.06881**	**C10H10O5**	**5-Hydroxy ferulate**	**[2M+K]1+**	**2.14**
			459.12613	**1520**	**459.12755**	**C17H23N4O9P**	**FMNH**	**[M+H]1+**	**-3.08**
			459.21397	1585	459.21435	C12H18O3	Jasmonate	[2M+K]1+	-0.83
E114F00h~E162F00h	**461.27**	**Positive**	**460.85626**	**1265**	**-**	**-**	**Unknown**	**-**	**-**
			461.17831	2252	461.18061	C24H28O9	6-Acetyl picropolin	[M+H]1+	-4.99
E129F00h~E484F00h	**463.27**	**Positive**	**463.06936**	**2619**	**-**	**-**	**Unknown**	**-**	**-**
			463.20935	**1080**	**463.20926**	**C23H36O7**	**Pravastatin**	**[M+K]1+**	**0.19**
			463.22452	1143	463.22586	C14H16N2	3,3'-Dimethyl benzidine	[2M+K]1+	-2.88
E114F00h~E480F00h	**471.27**	**Positive**	471.06798	840	471.06881	C21H20O10	Apigenin 7-O-β-glucoside	[M+K]1+	-1.76
			471.08987	**1540**	**471.08979**	**C21H20O11**	**Kaempferol-3-glucoside**	**[M+Na]1+**	**0.18**
E114F00h~E480F00h	**473.27**	**Positive**	**473.10587**	**1665**	**473.10544**	**C21H22O11**	**Pentahydroxychalcone 4'-O-glucoside**	**[M+Na]1+**	**0.92**
			473.17822	**4579**	**473.17567**	**C8H15N3O4**	**Acetyl citrulline**	**[2M+K]1+**	**5.38**
			473.19431	**1062**	**473.19361**	**C24H34O7**	**Phorbol 13-butanoate**	**[M+K]1+**	**1.47**
E137F00h~E485F00h	**485.27**	**Positive**	**485.14175**	**987**	**485.14197**	**C19H24N7O6**	**Tetrahydrofolate**	**[M+K]1+**	**-0.45**
			485.21509	**1099**	**485.21459**	**C25H34O8**	**Hydrocortisone succinate**	**[M+Na]1+**	**1.03**
			485.30255	**980**	**485.30277**	**C28H46O4**	**Di-N-Decyl phthalate**	**[M+K]1+**	**-0.45**
			485.36022	**1649**	**485.36254**	**C31H48O4**	**1-Hydroxyvitamin D3 diacetate**	**[M+H]1+**	**-4.77**
E114F00h~E333F00h	**489.9**	**Positive**	**489.95539**	**1514**	**-**	**-**	**Unknown**	**-**	**-**

			490.04523	**1050**	**-**	**-**	**Unknown**	**-**	**-**
			490.17718	**1873**	**490.17726**	**C22H33N3O5S**	**Formylmethionyl-leucyl-phenylalanine methyl ester**	**[M+K]1+**	**-0.15**
2N=10~2N=30	**493.27**	**Positive**	**493.13523**	**1316**	**493.13406**	**C23H24O12**	**Cicerin-7-O-glucoside**	**[M+H]1+**	**2.38**
			493.18332	**2337**	**493.18329**	**C26H30O8**	**Limonin**	**[M+Na]1+**	**0.06**
			493.20372	**1167**	**493.20457**	**C20H38O11**	**Octyl β-1,6-galactofuranosyl-α-glucopyranoside**	**[M+K]1+**	**-1.73**
			493.22002	**1014**	**493.21983**	**C24H38O8**	**18-Acetoxy-PGF2α-11-acetate**	**[M+K]1+**	**0.39**
2N=10~2N=20	**499.18**	**Positive**	**499.09780**	**1028**	**499.10011**	**C23H24O10**	**Afrormosin-7-O-glucoside**	**[M+K]1+**	**-4.62**
			499.11474	**2722**	**499.11632**	**C16H26N4O10S2**	**Bis-glutamyl cystine**	**[M+H]1+**	**-3.17**
			499.13487	**1264**	**499.13649**	**C24H28O9**	**6-Acetyl picropolin**	**[M+K]1+**	**-3.25**
			499.19366	**1500**	**499.19386**	**C25H32O9**	**2-Methoxyestrone 3-glucuronide**	**[M+Na]1+**	**-0.39**
			499.23090	**1122**	**499.23024**	**C26H36O8**	**Retinoyl β-glucuronide**	**[M+Na]1+**	**1.32**
2N=10~2N=20	**501.27**	**Positive**	**501.13774**	**1043**	**501.13674**	**C23H26O11**	**Homoferreirin-7-O-glucoside**	**[M+Na]1+**	**2.00**
			501.17347	**1295**	**501.17327**	**C21H34O11**	**Patrinoside**	**[M+K]1+**	**0.39**
E115F00h~E333F00h	**503.36**	**Positive**	**503.22510**	**1056**	**503.22756**	**C27H34O9**	**Verrucarin A**	**[M+H]1+**	**-4.89**
			503.26122	**1290**	**503.25919**	**C27H44O4S**	**7-Dehydrocholesterol-3-sulfate ester**	**[M+K]1+**	**4.03**
			503.33357	**2103**	**503.33431**	**C28H48O6**	**Brassinolide**	**[M+Na]1+**	**-1.47**
2N=20~2N=30	**512.27**	**Positive**	**512.05016**	**1474**	**-**	**-**	**Unknown**	**-**	**-**
			512.14597	**2082**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=20	**519.27**	**Positive**	**519.18399**	**1326**	**519.18609**	**C26H30O11**	**Simplexoside**	**[M+H]1+**	**-4.05**
			519.22025	**1121**	**-**	**-**	**Unknown**	**-**	**-**
			519.32940	**1079**	**-**	**-**	**Unknown**	**-**	**-**
2N=10~2N=20	527.27	Positive	527.15841	1634	527.15826	C18H32O16	Raffinose	[M+Na]1+	0.28
E114F00h~E137F00h	**531.17**	**Positive**	531.09036	2328	531.08994	C23H24O12	Cicerin-7-O-glucoside	[M+K]1+	0.79
			531.18381	923	531.18369	C25H32O11	Gibberellin 2-O-β-glucoside	[M+Na]1+	0.23
			531.25680	**1583**	**531.25886**	**C29H38O9**	**Uscharidin**	**[M+H]1+**	**-3.88**
E176F00h~E484F00h	**533.36**	**Positive**	**533.20008**	**1185**	**533.19934**	**C25H34O11**	**Gibberellin 2-O-β-glucoside**	**[M+Na]1+**	**1.40**
			533.27272	**1282**	**533.27451**	**C29H40O9**	**Calactin**	**[M+H]1+**	**-3.36**
			533.34509	**1190**	**533.34728**	**C31H48O7**	**1α,25-Dihydroxy-22-oxacholecalciferol 3-hemiglutarate**	**[M+H]1+**	**-4.11**
E137F00h~E160F00h	**543.27**	**Positive**	**543.13296**	**18401**	**543.13220**	**C18H32O16**	**Raffinose**	**[M+K]1+**	**1.40**
E137F00h~E160F00h	544.27	Positive	544.13612	3009	-	-	13C Isotope of Raffinose	[M+K]1+	-
E114F00h~E115F00h	545.27	Positive	545.13012	1317	-	-	41K Isotope of Raffinose	[M+K]1+	-
E137F00h~E160F00h	**553.36**	**Positive**	553.05768	1382	553.05655	C6H13O10P	6-Phospho gluconate	[2M+H]1+	2.04
			553.27812	**10018**	**-**	**-**	**Unknown**	**-**	**-**

E129F00h~E162F00h	**556**	**Positive**	**556.28020**	**1889**	**556.28000**	**C26H48NO7P**	**PC(18:3(9Z,12Z,15Z)/0:0)**	**[M+K]1+**	**0.36**
E114F00h~E162F00h	**557.36**	**Positive**	**557.12101**	**2379**	**-**	**-**	**Unknown**	**-**	**-**
			557.20039	**1575**	**-**	**-**	**Unknown**	**-**	**-**
			557.25217	**1361**	**557.25338**	**C34H36O7**	**Ingenol 3,20-Dibenzoate**	**[M+H]1+**	**-2.17**
2N=10~2N=30	**561.17**	**Positive**	**561.20986**	**1623**	**561.20966**	**C27H38O10**	**Trilobolide**	**[M+K]1+**	**0.36**
			561.30363	**1179**	**561.30356**	**C26H50O10**	**Tween 20**	**[M+K]1+**	**0.13**
E115F00h~E137F00h	**563.27**	**Positive**	**563.09567**	**1243**	**563.09487**	**C15H10O5**	**Apigenin**	**[2M+Na]1+**	**1.42**
			563.22579	**1237**	**563.22665**	**C14H18N2O3**	**Methohexital**	**[2M+K]1+**	**-1.52**
			563.24663	**1130**	**563.24869**	**C29H38O11**	**Eriocarpin**	**[M+H]1+**	**-3.66**
E333F00h~E484F00h	**566.09**	**Positive**	**565.99281**	**2705**	**-**	**-**	**Unknown**	**-**	**-**
			566.08931	**1360**	**566.09114**	**C17H27N3O13P2**	**dTDP-4-oxovancosamine**	**[M+Na]1+**	**-3.23**
E114F00h~E484F00h	**573.36**	**Positive**	**573.10094**	**1009**	**573.10276**	**C15H10O6**	**Kaempferol**	**[2M+H]1+**	**-3.17**
			573.19508	**1150**	**573.19264**	**C12H16NO7**	**N-Glucosyl nicotinate**	**[2M+H]1+**	**4.27**
			573.28438	**1548**	**573.28305**	**C11H26NO4P**	**Glyceryl phosphoryl choline**	**[2M+K]1+**	**2.31**
			573.41272	**1278**	**573.41287**	**C29H61NO6P**	**PC(O-18:0/O-3:1(2E))[U]**	**[M+Na]1+**	**-0.27**
E333F00h~E480F00h	587.36	Positive	587.13894	1087	587.13713	C26H28O14	Apigenin 7-O-[β-Apiosyl-(1->2)-β-Glucoside]	[M+Na]1+	3.08
2N=10~2N=20	**589.36**	**Positive**	**589.22647**	**6142**	**589.22796**	**C15H18O6**	**Tutin**	**[2M+H]1+**	**-2.52**
2N=10~2N=30	**591.45**	**Positive**	591.01295	863	591.01244	C6H13O10P	6-Phospho gluconate	[2M+K]1+	0.87
			591.22465	**817**	**591.22206**	**C7H16N8O4**	**Trimethylene tetra urea**	**[2M+K]1+**	**4.38**
			591.27777	**1120**	**591.27524**	**C30H48O7S**	**Tri terpenoid**	**[M+K]1+**	**4.28**
2N=10~2N=20	603.27	Positive	603.11118	4393	603.11151	C14H11N3O3S	Apigenin 7-O-[β-Apiosyl-(1->2)-β-Glucoside]	[M+K]1+	-0.54
2N=20~2N=30	**613.63**	**Positive**	**613.48268**	**2563**	**613.48265**	**C39H64O5**	**DG(18:3(6Z,9Z,12Z)/18:3(6Z,9Z,12Z)/0:0)**	**[M+H]1+**	**0.05**
E162F00h~E485F00h	**615.36**	**Positive**	**615.40255**	**2135**	**615.39963**	**C31H61O8P**	**PA(14:0/14:0)**	**[M+Na]1+**	**4.75**
2N=20~2N=30	**629.45**	**Positive**	**629.45284**	**1791**	**629.45418**	**C37H66O5**	**DG(16:1(9Z)/18:2(9Z,12Z)/0:0)**	**[M+K]1+**	**-2.13**
E114F00h~E260F00h	**633.36**	**Positive**	**633.11995**	**1190**	**633.12163**	**C27H30O15**	**Kaempferol 3-O-rhamnoside-7-O-glucoside**	**[M+K]1+**	**-2.66**
			633.48542	**884**	**633.48548**	**C37H70O5**	**DG(18:0/16:1(9Z)/0:0)**	**[M+K]1+**	**-0.10**
2N=20~2N=30	**635.54**	**Positive**	**635.41274**	**1437**	**635.41536**	**C36H58O9**	**Hederagenin-3-o-glucoside**	**[M+H]1+**	**-4.13**
			635.47635	**1476**	**635.47824**	**C20H31NO2**	**17β-Hydroxy-4,17-dimethyl-4-azaandrost-5-en-3-one**	**[2M+H]1+**	**-2.97**
			635.50124	**1203**	**635.50113**	**C37H72O5**	**DG(17:0/0:0/17:0)-D5**	**[M+K]1+**	**0.17**
2N=10~2N=20	**637.36**	**Positive**	**637.18891**	**7126**	**637.18994**	**C10H22NO7P**	**PC(0:0/2:0)[U]**	**[2M+K]1+**	**-1.62**
E114F00h~E115F00h	**644.8**	**Positive**	**644.67270**	**1633**	**-**	**-**	**Unknown**	**-**	**-**
			645.19781	**1101**	**645.19976**	**C36H34N2O7**	**Cancentrine**	**[M+K]1+**	**-3.03**
E260F00h~E480F00h	**671.36**	**Positive**	**671.36796**	**1116**	**671.37085**	**C20H28O3**	**15-PGA2**	**[2M+K]1+**	**-4.30**

			671.40577	970	671.40487	C34H65O8P	PA(17:0/14:1(9Z))	[M+K]1+	1.34
E114F00h~E480F00h	685.45	Positive	685.36411	1127	685.36268	C20H25N3O	Lysergate diethylamide	[2M+K]1+	2.08
E114F00h~E137F00h	722.9	Positive	723.19423	1795	723.19559	C12H22O11	Sucrose	[2M+K]1+	-1.88
E114F00h~E160F00h	745.63	Positive	745.62191	1147	745.62192	C22H43NO2	Anandamide (20:L, N-9)	[2M+K]1+	-0.01
2N=20~2N=30	784.63	Positive	784.58476	1515	784.58508	C44H82NO8P	PC(16:0/20:3(11E,14E,17E))[U]	[M+H]1+	-0.41
2N=10~2N=20	793.36	Positive	793.43590	744	793.43689	C42H64O14	Gypsogenin 3-O-rhamnosyl glucuronide	[M+H]1+	-1.24
			793.52235	1162	793.52266	C43H78O10	1-18:2-2-16:0-Monogalactosyl diacylglycerol	[M+K]1+	-0.39
E114F00h~E480F00h	794.54	Positive	794.50936	6723	794.50967	C42H78NO8P	PC(16:0/18:3(5E,9Z,12Z))[U]	[M+K]1+	-0.38
2N=10~2N=20	796.63	Positive	796.52557	7609	796.52532	C42H80NO8P	PC(16:0/18:2(2Z,4Z))	[M+K]1+	0.32
			796.60055	1475	796.59809	C44H88NO6P	PC(O-18:1(9Z)/O-18:1(9Z))	[M+K]1+	3.09
2N=10~2N=20	797.72	Positive	797.51793	14542	797.51742	C45H74O10	1,2 Di-(9Z,12Z,15Z-octadecatrienoyl)-3-O-β-galactosyl-sn-glycerol	[M+Na]1+	0.64
E114F00h~E162F00h	798.63	Positive	798.52029	7287	798.51984	C45H78NO6P	1-(8-[3]-Ladderane-octanyl)-2-(8-[3]-ladderane-octanyl)-sn-glycerophosphoethanolamine	[M+K]1+	0.57
E115F00h~E137F00h	815.54	Positive	815.48995	14486	815.48588	C24H36O4	3α-Hydroxy-12-oxo-5β-chol-9(11)-en-24-oate	[2M+K]1+	4.99
			815.49799	10883	815.49498	C41H76O12S	SQDG(16:0/16:1(11Z))	[M+Na]1+	3.70
E114F00h~E137F00h	816.54	Positive	816.49101	8132	816.49402	C44H76NO8P	PC(18:3(8E,10E,12E)/18:3(8E,10E,12E))[U]	[M+K]1+	-3.68
2N=10~2N=30	817.54	Positive	817.52373	3413	817.52266	C45H78O10	1-18:1-2-18:3-Monogalactosyl diacylglycerol	[M+K]1+	1.31
E137F00h~E162F00h	818.54	Positive	818.50962	4272	818.50967	C44H78NO8P	PC(16:1(9Z)/20:4(5Z,8Z,11Z,14Z)/0:0)	[M+K]1+	-0.05
E162F00h~E333F00h	819.54	Positive	819.39675	1159	819.39277	C41H64O14	Digoxin	[M+K]1+	4.86
			819.43014	1189	819.43380	C39H74O11P2	PPA(18:1(9Z)/18:1(9Z))	[M+K]1+	-4.47
			819.51147	2074	819.51466	C44H77O10P	PG(18:1(11Z)/20:4(5Z,8Z,11Z,14Z))	[M+Na]1+	-3.89
			819.53889	1016	819.53831	C45H80O10	1-18:1-2-18:2-Monogalactosyl diacylglycerol	[M+K]1+	0.71
E115F00h~E485F00h	820.54	Positive	820.52421	3772	820.52532	C44H80NO8P	PC(18:2(2E,4E)/18:2(2E,4E))	[M+K]1+	-1.35
2N=10~2N=20	821.54	Positive	821.52621	2110	821.53031	C44H79O10P	PG(18:0/20:4(5Z,8Z,11Z,14Z))	[M+Na]1+	-4.99
2N=10~2N=30	822.54	Positive	822.54088	1697	822.54097	C44H82NO8P	PC(18:0/18:3(9Z,12Z,15Z)/0:0)	[M+K]1+	-0.10
2N=10~2N=30	823.54	Positive	823.54340	1109	823.54596	C44H81O10P	PG(18:0/20:3(5Z,8Z,11Z))	[M+Na]1+	-3.11
2N=10~2N=30	828.54	Positive	828.47400	3812	828.47400	C42H69NO15	Leucomycin A3	[M+H]1+	0.00
			828.50795	1150	-	-	Unknown	-	-
E137F00h~E160F00h	829.54	Positive	829.48662	5045	829.48627	C45H74O11	1-18:3-2-18:3-Monogalactosyl diacylglycerol	[M+K]1+	0.42
E137F00h~E480F00h	861.54	Positive	861.47599	3282	861.47836	C25H34O6	21-Hydroxypregn-4-ene-3,20-dione hydrogen succinate	[2M+H]1+	-2.75
2N=10~2N=20	937.63	Positive	937.58463	924	937.58830	C51H84O15	1-18:3-2-18:3-Digalactosyl diacylglycerol	[M+H]1+	-3.92
2N=10~2N=30	941.54	Positive	941.35461	843	941.35686	C17H30N2O13	Galactosyl-3-(N-acetyl-β-galactosaminyl)-serine	[2M+H]1+	-2.39
			941.54941	1440	-	-	Unknown	-	-

2N=10~2N=30	953.63	Positive	953.56050	4967	953.55983	C49H86O15	1-16:0-2-18:3-Digalactosyl diacylglycerol	[M+K]1+	0.70
2N=10~2N=20	959.63	Positive	959.56943	1765	959.57025	C51H84O15	1-18:3-2-18:3-Digalactosyl diacylglycerol	[M+Na]1+	-0.85
E129F00h~E137F00h	975.63	Positive	975.54470	11590	975.54418	C51H84O15	1-18:3-2-18:3-Digalactosyl diacylglycerol	[M+K]1+	0.53

Table S10. List of annotated *m/z* signals where signal identities were confirmed by comparing MS^n fragmentation pattern with that of standard's

m/z	Ionization mode	Accurate *m/z*	Max. Intensity	Theoretical *m/z*	Molecular Formula	Identity	Adduct	PPM Error	MSI* Level of identification
116.09	Negative	116.07155	1962	116.07170	C5H11NO2	Valine	[M-H]1-	-1.31	1
118.09	Negative	118.05079	19614	118.05097	C4H9NO3	Threonine	[M-H]1-	-1.50	1
133.09	Negative	133.01404	689515	133.01425	C4H6O5	Malate	[M-H]1-	-1.56	1
135	Negative	135.02970	55697	135.02990	C4H8O5	Threonate	[M-H]1-	-1.47	1
147	Negative	147.04507	511	147.04515	C9H8O2	Cinnamate	[M-H]1-	-0.56	1
163	Negative	163.03983	29190	163.04007	C9H8O3	*p*-Coumarate	[M-H]1-	-1.46	1
179.09	Negative	179.03491	2291	179.03498	C9H8O4	Caffeate	[M-H]1-	-0.41	1
	Negative	179.05589	2268	179.05611	C6H12O6	Glucose	[M-H]1-	-1.25	1
185.09	Negative	184.98556	21029	184.98567	C3H7O7P	3-Phospho glycerate	[M-H]1-	-0.57	1
191.09	Negative	191.05585	164745	191.05611	C7H12O6	Quinate	[M-H]1-	-1.38	1
193.09	Negative	193.05061	13417	193.05063	C10H10O4	Ferulate	[M-H]1-	-0.12	1
259.18	Negative	259.02271	24036	259.02245	C6H13O9P	Glucose 6-phosphate	[M-H]1-	1.02	1
341.27	Negative	341.10886	210747	341.10894	C12H22O11	Sucrose	[M-H]1-	-0.23	1
377.27	Negative	377.08556	36887	377.08562	C12H22O11	Sucrose	[M+Cl]1-	-0.15	1
503.27	Negative	503.15904	1878	503.16176	C18H32O16	Raffinose	[M-H]1-	-5.41	1
539.27	Negative	539.13550	2797	539.13844	C18H32O16	Raffinose	[M+Cl]1-	-5.45	1
116	Positive	116.07030	9205	116.07061	C5H9NO2	Proline	[M+H]1+	-2.64	1
118.09	Positive	118.08587	1468640	118.08626	C5H11NO2	Both Valine and Betaine	[M+H]1+	-3.27	1
120.09	Positive	120.06515	37635	120.06552	C4H9NO3	Threonine	[M+H]1+	-3.09	1
132	Positive	132.10146	21097	132.10191	C6H13NO2	Leucine	[M+H]1+	-3.38	1
139.9	Positive	140.06789	56514	140.06820	C5H11NO2	Betaine	[M+Na]1+	-2.21	1
147.09	Positive	147.11243	3326	147.11281	C6H14N2O2	Lysine	[M+H]1+	-2.55	1
182	Positive	182.08037	1542	182.08117	C9H11NO3	Tyrosine	[M+H]1+	-4.40	1
203.18	Positive	203.05182	2016	203.05261	C6H12O6	Glucose	[M+Na]1+	-3.90	1
219.09	Positive	219.02584	46171	219.02655	C6H12O6	Glucose	[M+K]1+	-3.23	1
365.27	Positive	365.10457	21308	365.10544	C12H22O11	Sucrose	[M+Na]1+	-2.37	1
381.18	Positive	381.07882	821755	381.07937	C12H22O11	Sucrose	[M+K]1+	-1.45	1
527.27	Positive	527.15841	1634	527.15826	C18H32O16	Raffinose	[M+Na]1+	0.28	1
543.27	Positive	543.13296	18401	543.13220	C18H32O16	Raffinose	[M+K]1+	1.40	1

* Metabolomics Standards Initiative

Table S11. Contribution of metabolomic variables to the first canonical discriminant functions obtained for the studied ecotypes of *B. distachyon* (5 ecotypes, 60 replicates), *B. stacei* (3, 36) and *B. hybridum* (4, 48). Contribution values of positive and negative metabolites to the functions. (a) Metabolites not included in the discriminant analysis (see Figure 7). (b) Duplicate *m/z* signals with same metabolite annotations not included in the discriminant analysis (see Figure S1). * $p<0.05$.

Positives	Function 1		Function 2	Negatives	Function 1		Function 2
p556(a)	0.17135729	*	-0.03268181	n487.18(a)	0.10691284	*	0.05916933
p745.63(a)(b)	-0.11589141	*	0.06378592	n683.27(a)(b)	-0.10284352	*	-0.00752735
p821.54(a)	0.07819518	*	0.04588131	n534.09(a)	0.0909125	*	0.00448834
p644.8(a)	0.06599859	*	0.0324704	n449.09(a)(b)	0.08101284	*	-0.024566
p784.63(a)	0.06406575	*	0.0068279	n493.18(a)	-0.07917416	*	-0.05798212
p797.72(a)	-0.055852	*	-0.03887777	n773.36(a)	-0.07093755	*	0.06496141
p722.9(a)(b)	0.05001288	*	-0.01978989	n281.18	0.066872	*	-0.04709359
p793.36(a)	-0.04841338	*	-0.03791324	n541.27(a)(b)	-0.064112	*	-0.02159938
p531.17(a)	0.04745779	*	0.00035793	n711.45(a)(b)	0.06403728	*	-0.04741422
p563.27(a)	0.04705143	*	-0.01739839	n91.09(a)(b)	-0.06388151	*	0.04288624
p798.63(a)	-0.0424412	*	0.01930392	n564.27(a)(b)	-0.06056355	*	0.01539439
p671.36(a)	0.04182909	*	0.01524383	n385.18	-0.05910667	*	0.0413003
p185.09	0.03668609	*	0.00667615	n346.09	0.05868734	*	0.05402804
p74.09(a)	0.03543903	*	0.00283447	n420.18(a)	0.05716986	*	0.04242448
p161	-0.03533044	*	-0.00699052	n315.18	0.0570832	*	0.03625291
p829.54(a)	-0.03271584	*	0.02505552	n637.09(a)	0.05337797	*	0.04719185
p543.27	-0.03113857	*	-0.00918161	n831.63(a)	-0.0528396	*	-0.01228922
p425.27	-0.03018125	*	-0.0175534	n319.18	0.05219099	*	-0.01174737
p214.09	0.02912067	*	-0.00656418	n588.09(a)	0.05087734	*	-0.0392621
p822.54(a)	-0.02784804	*	-0.00830355	n183.09	-0.04969392	*	0.02863842

p959.63(a)	0.02773534	*	-0.02354728	n447.18(a)	0.04752689	*	0.01239004
p208.09	-0.02742153	*	-0.01300387	n567.17(a)(b)	0.04642749	*	-0.0412682
p259	0.02669739	*	-0.01271277	n237.09	0.04425317	*	-0.02893843
p375.18	-0.02651562	*	-0.02022726	n208.18	0.04419089	*	-0.02435153
p389.18	-0.026197	*	-0.00441676	n421.18(a)	0.04409848	*	0.04333511
p371.27	-0.02599031	*	-0.01742533	n364.18	-0.04384556	*	0.01160201
p251.09	0.02595212	*	-0.00436497	n236.09	0.04271356	*	0.02042987
p387.27	-0.02591783	*	-0.0170768	n168	0.04159374	*	0.01714706
p561.17	0.02540061	*	0.00341965	n837.63(a)	-0.04071231	*	0.0295045
p373.27	-0.02532623	*	-0.01741389	n218.09	0.0400986	*	0.01422365
p415.27	-0.02515384	*	-0.00858066	n367.18	-0.0381501	*	-0.01018694
p473.27	-0.02362285	*	-0.01995903	n397.09	0.03445392	*	0.01786764
p431.27	-0.02362083	*	-0.01891414	n431.18(a)	0.03408869	*	0.01622681
p144	-0.02319491	*	0.01195547	n563.27(a)(b)	-0.03300724	*	0.00163231
p275.08	0.02311835	*	-0.02001975	n323.18	0.02943576	*	0.00288512
p187.09(b)	0.02294846	*	-0.00524348	n241.09	0.02812934	*	0.00749078
p249.09	0.02291883	*	-0.00866178	n398.18	0.02631795	*	0.01309024
p455.18	-0.02260658	*	-0.02157215	n239.09(b)	0.0257073	*	-0.02437268
p401.27	-0.02245926	*	-0.01985136	n593.27(a)	0.02464305	*	0.01379899
p194.09	-0.02229803	*	-0.02123977	n269.18	0.02383524	*	-0.01365108
p461.27	-0.0217677	*	-0.01672509	n371.27	0.02367175	*	0.00699701
p432.27	-0.0215659	*	-0.01536629	n741.63(a)(b)	-0.02320561	*	0.01094665
p374.18	-0.02134043	*	-0.01742896	n158	-0.02273181	*	0.00217017
p445.27	-0.02066277	*	0.01472831	n355.18	0.02147256	*	0.0014226
p861.54(a)	-0.02036182	*	-0.01064722	n124	-0.02140078	*	-0.00086583
p545.27(b)	-0.02029911	*	0.01865338	n198	0.01735611	*	-0.01100114
p316.18	0.01997464	*	-0.00893347	n745.63(a)	0.01603167	*	-0.00187849
p413.27	-0.01991215	*	-0.00873967	n182.09	-0.01414265	*	0.01003864
p941.54(a)	0.0198647	*	0.00091987	n488.18(a)	-0.01353696	*	-0.0044062
p245.09	0.01907059	*	0.0042518	n419.09(a)	-0.01145159	*	0.00603576

p458.18	-0.01865699 *	-0.00532671	n311.18	-0.010112 *	0.00234456
p459.27	-0.01843039 *	-0.01662293	n440.18(a)	-0.00666115 *	0.00534058
p287.18	-0.01809892 *	-0.01514769	n429.18(a)	-0.00282702 *	-0.00188081
p107	-0.01662211 *	0.01444534	n640.9(a)	-0.0336556	-0.1509666
p485.27	-0.0165864 *	0.01135197	n463.18(a)	0.0215549	0.12164412 *
p147.09	0.01641064 *	-0.00786311	n455.18(a)	-0.01266939	0.12128073 *
p451.18(b)	0.01570822 *	0.00531923	n503.27(a)(b)	0.01092592	0.11386974 *
p314	0.01533471 *	0.00853629	n187.09	0.02342785	0.11365859 *
p263.08	0.01425238 *	-0.00827436	n163	0.03210545	-0.11349963 *
p343.18	-0.01417365 *	0.00059248	n191.09	0.03388844	0.10900074 *
p794.54	0.01383347 *	0.00874327	n174.09(b)	0.030881	0.10850088 *
p573.36(a)	0.01372934 *	0.01212334	n408.09(a)	0.00018872	-0.10739704 *
p246.09	0.01318767 *	-0.00346026	n203.09	0.00485209	0.10735808 *
p188.09	-0.01292403 *	-0.00731651	n103.09	0.0393604	0.10704601 *
p225	-0.01176425 *	0.00153209	n192.09(b)	0.03358449	0.10032185 *
p271.08	0.01165346 *	-0.009562	n116.09(b)	0.02953307	0.10000319 *
p236.09	-0.01144151 *	0.00825975	n173.09	0.02776066	0.09764381 *
p393.27	0.00963716 *	-0.00780288	n565.17(a)	-0.06795524	0.09750186 *
p227.09	0.00875656 *	-0.00325636	n204.09	0.00849998	0.09742876 *
p102	-0.00842455 *	-0.00764412	n118.09(b)	0.01923052	0.09674183 *
p319.18	0.00734949 *	-0.00575643	n407.18(a)	-0.05482895	0.09624705 *
p953.63(a)	0.0032139 *	0.0002241 *	n425.18(a)	-0.02807029	0.09499261 *
p591.45(a)	0.05910707	-0.12273571 *	n179.09	-0.01418672	-0.09447149 *
p828.54(a)	-0.00735892	0.09665576 *	n540.17(a)	-0.0377537	-0.09166627 *
p818.54(a)	-0.01863799	0.0940137 *	n379.18	-0.00422326	0.09144565 *
p296.18	0.01865014	0.08953956 *	n289.18	0.02979477	0.08864315 *
p823.54(a)	0.00785513	0.0876995 *	n135	0.03229688	0.08707913 *
p341.9	0.00718879	0.0805188 *	n89.09(a)	-0.04618635	0.08589293 *
p241	0.00780712	0.07898506 *	n341.27(b)	0.0022882	0.08534252 *
p587.36(a)(b)	-0.02470468	-0.07816338 *	n126	0.02603927	0.08445796 *

p139.9	-60.0996E-05	0.07639693	*	n259.18	0.00841547	0.08351186	*
p615.36(a)	-0.05184503	0.07278678	*	n221.09	-0.01897209	0.08203813	*
p685.45(a)	0.01842174	0.07173456	*	n223.09	0.03117499	0.08197337	*
p613.63(a)	-0.03080696	0.07123063	*	n277.18	0.0197725	0.08196764	*
p118.09	-0.0211047	0.0692034	*	n515.17(a)	0.07881158	0.08099477	*
p235.09	-0.01176515	0.06700429	*	n72.09(a)	0.04151713	0.08085707	*
p141.9	0.00867468	0.06663724	*	n207.09	0.00443291	0.08054853	*
p603.27(a)(b)	-0.01252154	-0.06611056	*	n623.17(a)	0.03909908	-0.07972835	*
p243	0.00653912	0.06572586	*	n342.18(b)	0.00505333	0.07896249	*
p796.63(a)	0.01780884	0.06554277	*	n142	0.01873417	0.07854977	*
p119.09	-0.01855705	0.06426201	*	n129.09	-0.02048275	0.0782987	*
p442.9	-0.00707965	0.05958822	*	n117	-0.00036284	0.07786907	*
p156(b)	-0.01589888	0.05883721	*	n145.09	0.03181791	0.07785151	*
p157(b)	-0.01271255	0.05842928	*	n437.18(a)	-0.02854968	0.0768511	*
p589.36(a)	-0.0212538	-0.05818232	*	n134.09(b)	0.03747538	0.07650159	*
p637.36(a)	-0.02656575	0.05755332	*	n119	-0.0045675	0.07605684	*
p158(b)	-0.01111817	0.0566398	*	n193.09	0.01936176	0.07591462	*
p975.63(a)	0.02493056	0.0564019	*	n133.09	0.03943679	0.07582015	*
p257.08	-0.01157654	0.05552115	*	n195.18	-0.03599773	0.075591	*
p268.18	0.01605075	-0.05157071	*	n387.18	-0.01758294	0.0754981	*
p303.18	-0.04913525	-0.04941833	*	n144.09	0.02278051	0.07467059	*
p635.54(a)	0.00127512	-0.04657567	*	n271	0.01878765	0.07448961	*
p359.18	0.0179383	0.04466575	*	n232.09	0.01972189	0.07391333	*
p138.09	0.0062768	-0.04399293	*	n229.09	0.02019992	0.07377056	*
p544.27(a)(b)	-0.01502589	-0.04176155	*	n413.18(a)	-0.00102123	0.07279405	*
p381.18	0.00667761	-0.04136004	*	n359.18(b)	0.01672865	0.0718037	*
p244.18	-0.00715239	0.04129091	*	n194.09	0.02392555	0.07154963	*
p817.54(a)	-0.02658129	0.0408488	*	n222.09	0.02347324	0.07150948	*
p320.18	-0.00615287	0.03973365	*	n377.27(b)	-0.00581768	0.07146513	*
p820.54(a)	-0.01623826	0.03973056	*	n216.09	0.00763139	0.0710507	*

p98(a)	-0.03101881	-0.03880071	*	n217.18(b)	0.00162752	0.07099585	*
p123	-0.01395276	0.03835744	*	n343.18	-0.00260522	0.07036414	*
p269.18	0.01104821	-0.03828728	*	n327.18	0.01990253	0.06989065	*
p557.36(a)	-0.00126497	0.0379244	*	n104.09(b)	-0.01102211	0.06920225	*
p351.18	0.00078614	-0.03753876	*	n185.09	0.02483926	0.06861393	*
p383.18(b)	0.00400772	-0.03723309	*	n213.09	0.02349962	0.06846964	*
p463.27	-0.01240458	-0.0372161	*	n382.18	0.02375535	-0.06828923	*
p382.18(b)	0.00653646	-0.03640474	*	n380.18	-0.02310335	0.06820798	*
p355.18(b)	-0.01762868	-0.03632206	*	n231.09	0.02470378	0.06794703	*
p527.27(b)	-0.03039452	-0.03588899	*	n123	-0.00142824	0.06726252	*
p326	-0.00401082	0.03583792	*	n329.18	0.02361396	0.06709435	*
p365.27(b)	-0.01881622	-0.03533682	*	n479.18(a)	-0.03837487	0.06706999	*
p315	-0.00131623	0.03406258	*	n247.09	0.02274443	-0.06677487	*
p217.18	-0.00414669	-0.03386248	*	n475.09	0.00908495	0.06642628	*
p501.27	-0.02081549	-0.03304894	*	n210.09	0.002316	-0.06623342	*
p123.9	-0.02159087	0.03191294	*	n101.09	0.00838092	0.06576783	*
p425.9	-0.00166877	0.03190432	*	n309.18	0.0123491	0.06500331	*
p384.18	-0.00528392	-0.03164316	*	n245.09	0.01856076	0.06497199	*
p299.18	-0.00798639	-0.03102332	*	n151	-0.01498735	0.06256087	*
p815.54(a)	-0.0205414	0.03063717	*	n535.27(a)	-0.03615952	-0.0623386	*
p441.27	-0.01681731	-0.03037066	*	n815.72(a)	-0.0496955	0.06158677	*
p141	-0.02024014	0.03025257	*	n121	-0.04116031	0.06071729	*
p111.54	-0.01773672	0.03021229	*	n211.09	0.00406941	-0.0600454	*
p307.18	-0.00060585	-0.02984555	*	n201.09	0.00186953	0.05986275	*
p323.18	-0.00786287	-0.02958797	*	n279.18	0.00486933	0.0597708	*
p182	-0.0022156	0.02949432	*	n212.09	0.00408485	-0.05970942	*
p283.18	-0.01594478	-0.02929479	*	n566.27(a)	-0.02671568	-0.05964453	*
p512.27	-0.0043626	-0.02857765	*	n423.18(a)	-0.00825993	0.05879851	*
p367.18	0.00487315	-0.02845452	*	n278.18	0.01254602	0.05874761	*
p215	0.00801344	-0.02838471	*	n389.18	0.00929836	0.05815306	*

p385.18	-0.02151347	-0.02837774	*	n71.09(a)	0.05569231	0.05809948	*
p489.9	-0.00622776	0.02775259	*	n459.09(a)	-0.01246579	0.05746197	*
p377.27(b)	0.00164105	-0.02763185	*	n107.09	-0.02446038	0.05741966	*
p424.18	0.00027382	-0.02754791	*	n253.09	0.02649381	0.05708799	*
p503.36	-0.0179622	-0.02715203	*	n266.08	0.02004362	-0.05698637	*
p366.27(b)	-0.02445893	-0.02660359	*	n388.18	0.00748036	0.05653227	*
p437.27	0.00245714	-0.02649755	*	n298.18	0.00776899	0.05627399	*
p116	-0.00944816	0.02562608	*	n105.09	0.03843572	0.05584997	*
p120.09	-0.01469729	0.02543706	*	n316.18	0.04461231	0.05425913	*
p345.18	-0.02143302	-0.0254367	*	n597.17(a)	-0.02596052	0.0540724	*
p219.09	0.00392677	-0.02539782	*	n513.17(a)(b)	0.01067602	0.05390167	*
p229.18	-0.01409067	-0.02511075	*	n152.09	-0.01139991	-0.05373961	*
p127.09	0.00778045	0.02475968	*	n297.18	0.0063085	0.05359655	*
p132.44(b)	-0.01382071	0.02462501	*	n215.09(b)	-0.00627284	0.05358247	*
p139	-0.00179733	-0.02444608	*	n228.09	-0.00083312	0.05351008	*
p132	-0.01266488	0.02428972	*	n471.18(a)	-0.00793498	0.05288463	*
p286.08(b)	0.01700757	0.02408596	*	n793.72(a)	-0.03184692	0.05280508	*
p150	-0.00339609	0.0240551	*	n435.18	0.05096564	-0.05271241	*
p533.36	0.00606747	-0.02359665	*	n393.09	0.02536316	0.05269626	*
p392	0.0059922	-0.02327506	*	n197.18	-0.01551853	0.05124483	*
p471.27	-0.01911026	-0.02309861	*	n87.09(a)	0.02000473	0.0506425	*
p553.36(a)	0.01140363	-0.02276638	*	n147	-0.0175082	-0.05036831	*
p357.27	-0.02044951	-0.02271193	*	n369.09	-0.00618641	0.04965657	*
p261.18	-0.01258507	-0.0227078	*	n344.09	0.03273682	-0.04940203	*
p629.45	0.00138415	0.02253766	*	n347.09	0.04195793	0.04922704	*
p279.18	0.01199126	-0.02234593	*	n340.09	0.03897618	-0.04916661	*
p457.27	-0.02158574	-0.02215635	*	n88.09(a)	0.01755829	0.04907508	*
p499.18	-0.01646321	-0.02208113	*	n303.18	0.03263171	0.04892497	*
p294.18	-0.01401933	-0.02168967	*	n274.08	0.04087023	0.04860858	*
p149.54	-0.00710405	0.02159323	*	n136	0.03812048	-0.04851476	*

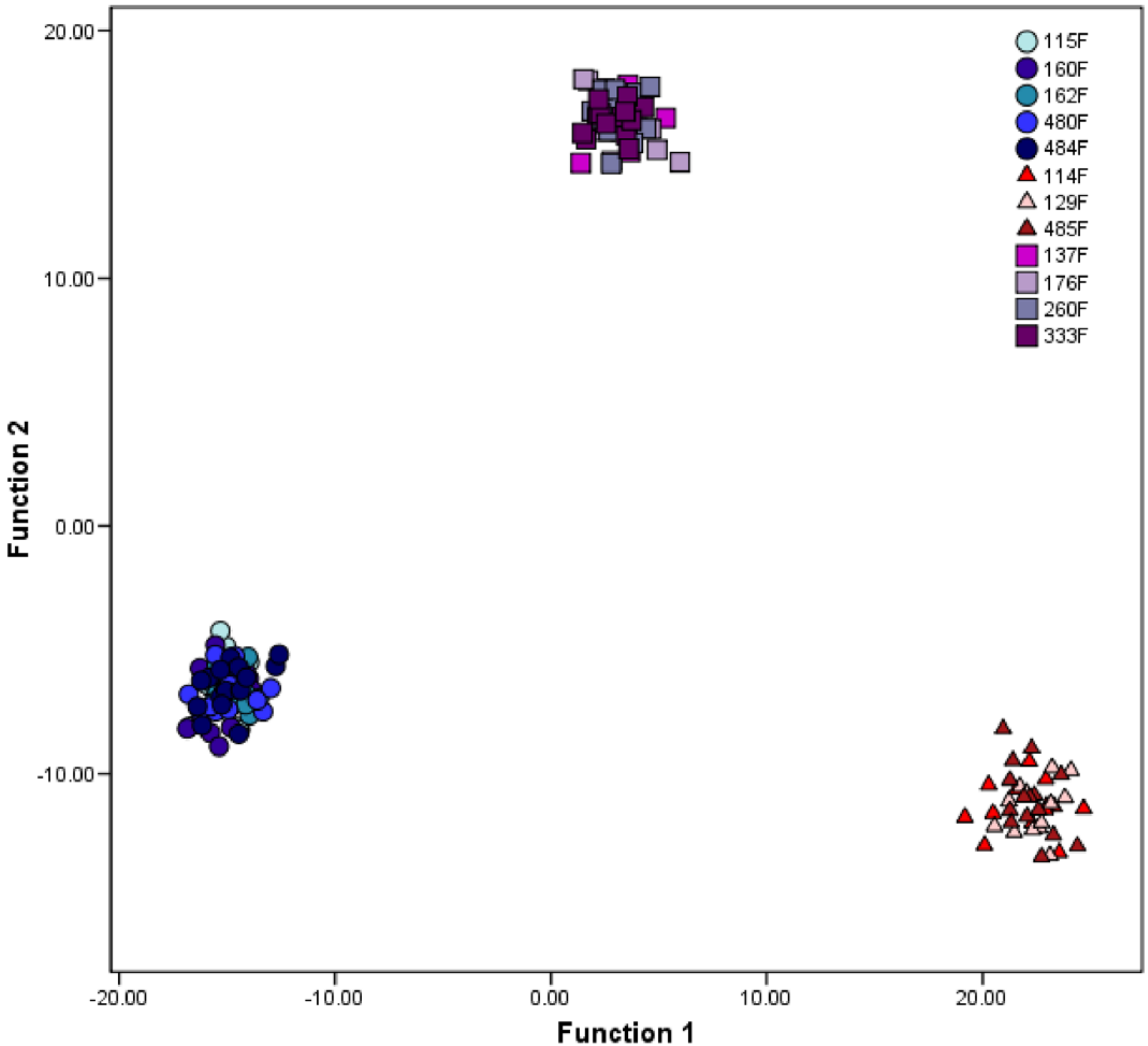
p282.18	-0.00743525	-0.02157041	*	n181.09	0.04275054	0.04783606	*
p816.54(a)	0.00055569	0.0214223	*	n362.18	0.01801329	0.04738684	*
p264.18(b)	-0.01390805	-0.02115437	*	n453.18(a)	-0.00567966	0.04698278	*
p295.18	-0.01017743	-0.02107792	*	n143.09	-0.01264473	0.0468813	*
p173	-0.0088152	-0.02082232	*	n171	0.02081014	0.04534125	*
p128	0.0068011	0.02076778	*	n251.18	0.04387136	0.04490878	*
p62.09(a)	0.00341026	-0.02065367	*	n184.09	-0.01123123	0.04467933	*
p364.09	-0.0037785	0.02061619	*	n224.09(b)	0.03869826	0.04406147	*
p176	0.01526482	-0.02039539	*	n132.09	-0.02962011	0.04342782	*
p203.18(b)	-0.01547632	-0.02029161	*	n521(a)(b)	60.2714E-05	-0.04162318	*
p184	-0.00493959	0.0201031	*	n257.08	-0.00248912	0.04104685	*
p233.18	-0.01066595	-0.01998763	*	n255.27	-0.00951153	0.0402138	*
p84.09(a)	0.00306756	0.01997187	*	n295.18	0.00651354	0.03989269	*
p224.09	-0.00816055	-0.01959942	*	n819.63(a)	0.0169355	0.03972643	*
p278.18(b)	0.0154575	-0.01930246	*	n743.63(a)	-0.0045642	0.03957746	*
p191	-0.00630511	0.01883918	*	n469.18(a)(b)	-0.00269068	0.03851735	*
p159	-0.00532332	0.01863778	*	n240.09	0.03552984	-0.0382373	*
p937.63(a)(b)	0.0172166	-0.0181005	*	n73.09(a)	0.00525237	0.03761704	*
p273.18(b)	-0.01518347	0.01796049	*	n719.63(a)	0.02130188	0.03758092	*
p395.18	0.00668088	-0.01758732	*	n220.09(b)	-0.01280534	-0.0373915	*
p566.09	0.00377589	-0.01749029	*	n263.18	0.01804128	-0.03682512	*
p277.18	0.01683382	-0.017469	*	n146.09	-0.01841513	0.03644474	*
p145	-0.01454418	0.01744678	*	n326.18	-0.01679075	0.03586411	*
p211.09	0.01670983	-0.01742886	*	n293.27	-0.01212114	0.03555941	*
p114	-0.00871498	-0.01550419	*	n102.09	-0.01811975	0.03527974	*
p819.54(a)	-0.00343397	0.01544675	*	n148.09	-0.01425118	0.03515105	*
p633.36(a)	-0.01071156	0.01535235	*	n481.27(a)	0.01109477	0.03368782	*
p258.18	0.01142149	0.01517629	*	n267.18	0.00578409	0.03331052	*
p329.18	0.00718366	-0.01507546	*	n443.18(a)	0.00131349	0.03201525	*
p160	-0.01225392	-0.0144293	*	n337.09	-0.00948511	0.0313457	*

p183.09	0.0061735	0.01439279	*	n381.18	-0.02948856	0.0297257	*
p241.72	-0.00752764	0.01437226	*	n157	-0.01703734	0.0286304	*
p255.18	0.01406834	-0.01415898	*	n510(a)	-0.00357686	-0.02817446	*
p449.18	0.00995409	0.01402452	*	n100	-0.0243482	0.02771759	*
p175	-0.0032051	-0.01379232	*	n601.17(a)	0.02118683	-0.0271685	*
p237.09	-0.00127061	0.01374697	*	n139	-0.00950263	0.02701138	*
p113.45	-0.0007686	-0.0130095	*	n138	0.01237562	-0.02552221	*
p195.09	-0.00751466	-0.01291693	*	n125	0.0032058	-0.02465505	*
p391	0.00718986	0.01250418	*	n312.18	-0.0084258	0.02462516	*
p313.18	0.01017652	-0.01222449	*	n539.27(a)(b)	-0.01919355	-0.02183815	*
p312.08	0.0083926	0.01150936	*	n265.18	-0.00726031	0.01760863	*
p210	-0.01036481	0.01112708	*	n483.27(a)	-0.00560975	0.01661438	*
p231.09	0.01035481	-0.0110806	*	n165	-0.01307494	-0.01572853	*
p106	-0.01057506	-0.01094875	*	n199.09	0.00973433	0.01531145	*
p519.27	-0.00561853	0.01036538	*	n349.09	-0.01219379	0.01425127	*
p58.09(a)(b)	-0.00474148	0.01029416	*	n427.18(a)	-0.00271607	-0.01186634	*
p493.27	0.00805664	-0.01001674	*	n399.18(a)	0.00245719	-0.0076831	*

Table S12. Statistics of 16 metabolites and significance tests of their mean values in *Brachypodium distachyon*, *B. stacei* and *B. hybridum*. N, number of ecotypic samples analysed. ANOVA (F; d.f. 2) test of variables used for comparisons among species. Superscripts denote Tukey pairwise comparisons between species; means with the same letter do not differ significantly ($p<0.05$).

Species	p139.9	p147.09	p182	p214.09	p235.09	p296.18	p381.18	p816.54	n135	n163	n179.09	n203.09	n281.18	n315.18	n346.09	n385.18
B. distachyon																
N	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75	75
Minimum	19200	992	7500	4210	9750	1990	212000	53800	1530	1850	817	20400	7880	7630	3210	7660
Maximum	61800	3370	67100	21600	45300	9660	689000	198000	5620	18800	3460	101000	40100	51700	22100	56000
Mean	36630,7^{b}	1920,7^{b}	23239,9^{b}	9694,1^{c}	21650^{b}	4980,5^{c}	403173,3^{b}	123758,7^{b}	3302,8^{a}	8027,1^{a}	2023,5^{b}	42169,3^{b}	18838,3^{c}	20624,4^{c}	10630,9^{c}	22654^{a}
Std. Deviation.	9309,1	575,1	11833,8	3591,3	6625,5	1572,3	90742,6	31246,4	946,3	2984,9	653,6	12740,1	6467,3	7370,2	3846,6	9717,9
B. stacei																
N	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45
Minimum	25400	1160	8900	6820	9680	3320	207000	104000	1530	5470	954	16200	29300	20400	7220	3110
Maximum	92100	4860	64700	20100	46100	21400	561000	231000	7940	28800	4200	66000	228000	84600	63800	15000
Mean	57448,9^{a}	2225,6^{b}	30130,2^{a}	13670,9^{b}	28952,9^{a}	11051,3^{a}	327288,9^{c}	162911,1^{a}	3556,4^{a}	17264^{b}	2352,3^{a}	27671,1^{c}	93328,9^{a}	46406,7^{b}	22729,3^{b}	6548^{c}
Std. Deviation.	14966,7	732,9	11627,2	3771,383	7632,292	3429,171	73826,462	35832,8	1451,9	5631	649,7	11277,3	37823,9	17138,8	10327,4	2676,4
B. hybridum																
N	59	59	59	59	59	59	59	59	59	59	59	59	59	59	59	59
Minimum	7570	1230	5630	6790	8270	2880	231000	77900	1980	1490	730	17400	20700	12600	7570	4580
Maximum	66200	5540	50800	30800	28900	10900	698000	257000	20800	21700	2260	102000	148000	151000	67100	25000
Mean	31426,6^{c}	2641,2^{a}	20013,9^{b}	16988,3^{a}	15325,4^{c}	5996,4^{b}	463932,2^{a}	175786,4^{a}	8053,2^{b}	8982,4^{a}	1342,7^{c}	55983^{a}	71940,7^{b}	59771,2^{a}	32733,2^{a}	11138,6^{b}
Std. Deviation.	11055,32	1021,6	9612,4	6091,799	4122,737	1570,903	129507,8	46207,8^{a}	4531,9	4020,2	408,3	18316,1	35929,7	26458	12993,3	4461,2
F	71,1	13,9	10,8	41,9	61,5	114,7	23	34,2	56	78	42,1	48,8	113	81,1	92,2	88,2
p	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.002	<0.003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Fig. S1


20.00
10.00
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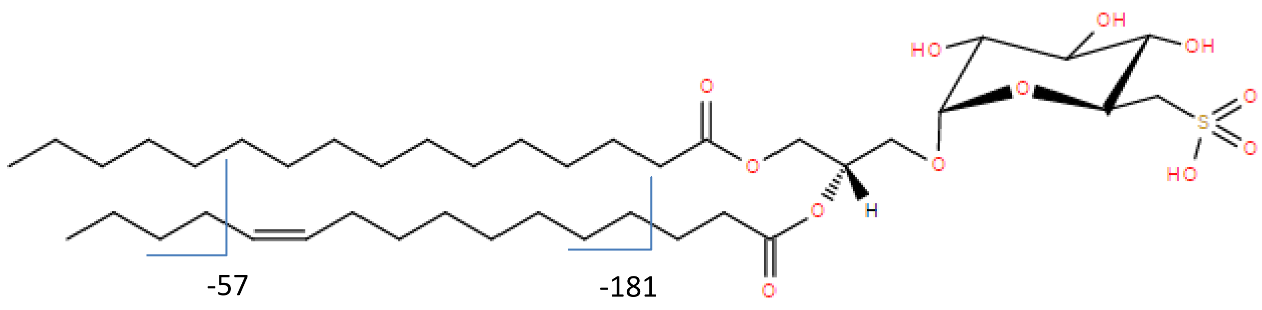
-10.00
-20.00
-10.00
0.00
10.00
20.00
Function 1
Function 2
115F
160F
162F
480F
484F
114F
129F
485F
137F
176F
260F
333F

Fig. S2

***m/z* 815.54 [M+Na]$^{1+}$ (SQDG)**



815.54 - (C_4H_9) 57.27 = 758.27
815.54 - ($C_{13}H_{25}$) 181.36 = 634.18