**Supplementary Materials**

**Phenolic profile dynamics during grain development in hull-less food barley genotypes with varying grain colors**

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| **Table S1.** Thousand Grain Weight (TGW) of four barley genotypes at different maturation stages. | | | | |
| **Genotype** | **Stage** | **TGW (g)** | | |
| DHL-190849  (Yellow) | Milky | 30.15 | ± | 0.65 |
| Softy | 38.14 | ± | 0.16 |
| PM | 40.66 | ± | 0.30 |
| Harvest | 40.06 | ± | 0.24 |
| Rajapani®  (Blue) | Milky | 20.96 | ± | 0.23 |
| Softy | 31.84 | ± | 0.46 |
| PM | 40.41 | ± | 0.98 |
| Harvest | 40.95 | ± | 2.46 |
| DHL-151340  (Purple) | Milky | 34.91 | ± | 0.92 |
| Softy | 43.98 | ± | 0.60 |
| PM | 49.73 | ± | 0.88 |
| Harvest | 48.72 | ± | 1.76 |
| DHL-191250  (Black) | Milky | 37.19 | ± | 2.38 |
| Softy | 42.71 | ± | 1.82 |
| PM | 51.60 | ± | 1.81 |
| Harvest | 50.92 | ± | 1.42 |
| Results are presented as the mean ± standard deviation. PM: Physiological maturity | | | | |

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| **Table S2**. SRM conditions and MS2 fragments used for the quantification and identification of phenolic compounds in barley samples. | | | | | | | | |
|  | **[M-H]-/+**  **(*m/z*)** | | **SRM transitiona** | **Cone Voltage (V)** | **Collision Energy (eV)** | **MS2 fragment spectrumb** | **Quantified as** | **Identification level c** |
| **Flavan-3-ols** |  |  | |  |  |  |  |  |
| Catechin | 289 | 245 | | 45 | 15 | 245, 205, 151 | Catechin | Std |
| Catechin-glucoside | 451 | 289 | | 45 | 15 | 289 | Catechin | Tent |
| Procyanidin B3 (C-C) | 577 | 289 | | 45 | 20 | 425,289 | Catechin | Tent |
| Procyanidin B2 | 577 | 289 | | 45 | 20 | 289 | Catechin | Tent |
| Prodelphinidin B4 (GC-C) | 593 | 289 | | 45 | 20 | 289 | Catechin | Tent |
| Prodelphinidin B3 (GC-C) | 593 | 289 | | 45 | 20 | 467, 289 | Catechin | Tent |
| Procyanidin-diglucoside | 613 | 451 | | 45 | 15 | 451, 289 | Catechin | Tent |
| Procyanidin C2 (C-C-C) | 865 | 289 | | 60 | 30 | 577, 289 | Catechin | Tent |
| C-C-GC/GC-C-C | 881 | 577 | | 60 | 25 | 577, 289, 245 | Catechin | Tent |
| C-GC-C | 881 | 593 | | 60 | 25 | 593 | Catechin | Tent |
| **Phenolic Acids and Aldehydes** |  |  | |  |  |  |  |  |
| Ferulic acid (*trans*) | 193 | 134 | | 30 | 15 | 178, 134, 149 | Ferulic acid (*trans*) | Std |
| Ferulic acid (*cis*) | 193 | 134 | | 30 | 15 | 178, 134, 149 | Ferulic acid (*trans*) | Tent |
| Iso-Ferulic acid | 193 | 134 | | 30 | 15 | 178, 134, 149 | Ferulic acid (*trans*) | Tent |
| Di-ferulic acid I | 385 | 341 | | 40 | 15 | 341, 326, 282, 297 | Ferulic acid (*trans*) | Tent |
| Di-ferulic acid II | 385 | 341 | | 40 | 15 | 341, 326, 297, 282, 267 | Ferulic acid (*trans*) | Tent |
| Di-ferulic acid III | 385 | 341 | | 40 | 15 | 341, 326, 282 | Ferulic acid (*trans*) | Tent |
| Di-ferulic acid IV | 385 | 341 | | 40 | 15 | 341, 193, 178, 149, 134 | Ferulic acid (*trans*) | Tent |
| Di-ferulic acid (decarboxylated form) | 341 | 282 | | 40 | 15 | 326, 282, 267, 297 | Ferulic acid (*trans*) | Tent |
| Tri-ferulic acid I | 577 | 355 | | 50 | 20 | 533, 489, 355, 311, 193 | Ferulic acid (*trans*) | Tent |
| Tri-ferulic acid II | 577 | 355 | | 50 | 20 | 355, 193 | Ferulic acid (*trans*) | Tent |
| *p*-Coumaric acid (*trans*) | 163 | 119 | | 35 | 10 | 119, 93 | *p*-Coumaric acid (*trans*) | Std |
| Coumaric acid (*m*-CoA or *p*-CoA cis) | 163 | 119 | | 35 | 10 | 119, 93 | *p*-Coumaric acid *(trans*) | Tent |
| Sinapic acid | 223 | 164 | | 35 | 15 | 208, 164, 149 | Sinapic acid | Std |
| Caffeic acid | 179 | 135 | | 20 | 12 | 135 | Caffeic acid | Std |
| Sinapoyl-hexose | 385 | 223 | | 60 | 25 | 223, 205 | Sinapic acid | Tent |
| Cinnamic acid | 147 | 103 | | 45 | 15 | 103 | *p*-Coumaric acid *(trans*) | Tent |
| Feruloyl-pentose | 325 | 193 | | 40 | 10 | 193, 149, 134 | Ferulic acid (*trans*) | Tent |
| *p*-Hydroxybenzoic acid | 137 | 93 | | 30 | 15 | 93 | *p*-hydroxybenzoic acid | Std |
| 2.4-Dihydroxybenzoic acid | 153 | 109 | | 45 | 15 | 109 | *p*-hydroxybenzoic acid | Tent |
| Vanillic acid | 167 | 123 | | 30 | 10 | 152, 123 | Vanillic acid | Std |
| Syringic acid | 197 | 182 | | 30 | 10 | 182, 153 | Syringic acid | Std |
| Syringaldehyde | 181 | 166 | | 30 | 15 | 166, 151 | *p*-Coumaric acid *(trans*) | Tent |
| **Flavone glycosides** |  |  | |  |  |  |  |  |
| Isoscoparin-7-O-glucoside | 623 | 341 | | 60 | 20 | 461, 341 | Apigenin-7-*O*-glucoside | Tent |
| Luteolin-7-O-glucoside | 447 | 285 | | 45 | 25 | 285 | Luteolin-7-*O*-glucoside | Std |
| **Anthocyanins \*** |  |  | |  |  |  |  |  |
| Cyanidin-glucoside | 449 | 287 | | 40 | 20 | 287 | Cyanidin-3-*O*-glucoside | Std |
| Cyanidin-acetyl-glucoside | 491 | 287 | | 40 | 30 | 287 | Cyanidin-3-*O*-glucoside | Tent |
| Cyanidin-malonylglucoside | 535 | 287 | | 40 | 15 | 287 | Cyanidin-3-*O*-glucoside | Tent |
| Cyanidin-dimalonylglucoside | 621 | 287 | | 40 | 20 | 287 | Cyanidin-3-*O*-glucoside | Tent |
| Pelargonidin-glucoside | 433 | 271 | | 40 | 20 | 271 | Cyanidin-3-*O*-glucoside | Tent |
| Pelargonidin-malonylglucoside | 519 | 271 | | 40 | 25 | 271 | Cyanidin-3-*O*-glucoside | Tent |
| Pelargonidin-dimalonylglucoside | 605 | 271 | | 40 | 20 | 271 | Cyanidin-3-*O*-glucoside | Tent |
| Peonidin-glucoside | 463 | 301 | | 40 | 20 | 301 | Cyanidin-3-*O*-glucoside | Tent |
| Peonidin-malonylglucoside | 549 | 301 | | 40 | 20 | 301 | Cyanidin-3-*O*-glucoside | Tent |
| Peonidin-dimalonylglucoside | 635 | 301 | | 40 | 20 | 301 | Cyanidin-3-*O*-glucoside | Tent |
| Delphinidin-glucoside | 465 | 303 | | 40 | 20 | 303 | Cyanidin-3-*O*-glucoside | Tent |
| Delphinidin-malonylglucoside | 551 | 303 | | 40 | 20 | 303 | Cyanidin-3-*O*-glucoside | Tent |
| Delphinidin-dimalonylglucoside | 637 | 303 | | 40 | 20 | 303 | Cyanidin-3-*O*-glucoside | Tent |
| Delphinidin-rutinisode | 611 | 303 | | 40 | 20 | 303 | Cyanidin-3-*O*-glucoside | Tent |
| Petunidin-malonylglucoside | 565 | 317 | | 40 | 20 | 317 | Cyanidin-3-*O*-glucoside | Tent |
| Petunidin-dimalonylglucoside | 651 | 317 | | 40 | 20 | 317 | Cyanidin-3-*O*-glucoside | Tent |
| Petunidin-rutinisode | 625 | 317 | | 40 | 20 | 317 | Cyanidin-3-*O*-glucoside | Tent |
| Petunidin-hexoside-hexoside | 691 | 317 | | 40 | 20 | 317 | Cyanidin-3-*O*-glucoside | Tent |
| Malvidin- malonylglucoside | 579 | 331 | | 40 | 20 | 331 | Cyanidin-3-*O*-glucoside | Tent |
| Malvidin-dimalonylglucoside | 665 | 331 | | 40 | 25 | 331 | Cyanidin-3-*O*-glucoside | Tent |
| Malvidin-hexoside-hexoside | 655 | 331 | | 40 | 15 | 331 | Cyanidin-3-*O*-glucoside | Tent |
| aSRM transition: selected reaction monitoring used for quantification. b MS2 fragment: fragmentation products used for identification. c Std: Standard in which the phenolic has been quantified. When the phenolic was not quantified with its own standard, the quantification was tentative (Tent). \*Anthocyanins were analysed in positive ion mode. | | | | | | | | |

**Table S3.** Anthocyanins contents (µg/g)in four barley genotypes at different stages of maturation.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Rajapani® (Blue)** | | | | | | | | **DHL-151340 (Purple)** | | | | | | | |
|  | **Milky** | | **Softy** | | **PM** | | **Harvest** | | **Milky** | | **Softy** | | **PM** | | **Harvest** | |
| Cyanidin-glucoside | 0.024 | ± 0.0042 | 0.229 | ± 0.0142 | 0.081 | ± 0.0025 | 0.017 | ± 0.0009 | 1.970 | ± 0.1483 | 3.987 | ± 0.1187 | 6.783 | ± 0.1197 | 0.760 | ± 0.0154 |
| Cyanidin-acetyl-glucoside | nd | | 0.008 | ± 0.0001 | 0.005 | ± 0.0005 | nd | | 0.188 | ± 0.0120 | 0.478 | ± 0.0267 | 0.539 | ± 0.0253 | 0.072 | ± 0.0020 |
| Cyanidin-malonylglucoside | 0.107 | ± 0.0058 | 0.771 | ± 0.0427 | 0.806 | ± 0.0277 | 0.131 | ± 0.0020 | 16.179 | ± 0.5844 | 47.423 | ± 1.2006 | 53.368 | ± 1.3582 | 7.021 | ± 0.1653 |
| Cyanidin-dimalonylglucoside | 0.163 | ± 0.0177 | 0.941 | ± 0.0451 | 4.465 | ± 0.1316 | 0.705 | ± 0.0251 | 85.540 | ± 1.8139 | 249.680 | ± 5.0248 | 262.911 | ± 3.2838 | 19.502 | ± 0.2096 |
| Pelargonidin-glucoside | nd | | 0.004 | ± 0.0005 | nd | | nd | | 0.033 | ± 0.0012 | 0.147 | ± 0.0133 | 0.202 | ± 0.0082 | 0.045 | ± 0.0063 |
| Pelargonidin-malonylglucoside | 0.008 | ± 0.0004 | 0.062 | ± 0.0014 | 0.070 | ± 0.0027 | 0.012 | ± 0.0003 | 0.514 | ± 0.0195 | 3.381 | ± 0.1965 | 3.445 | ± 0.2110 | 0.592 | ± 0.0258 |
| Pelargonidin-dimalonylglucoside | 0.004 | ± 0.0003 | 0.033 | ± 0.0010 | 0.183 | ± 0.0044 | 0.030 | ± 0.0016 | 1.399 | ± 0.1360 | 11.046 | ± 0.2629 | 10.149 | ± 0.4383 | 0.960 | ± 0.0596 |
| Peonidin-glucoside | nd | | 0.013 | ± 0.0008 | nd | | nd | | 0.222 | ± 0.0404 | 0.493 | ± 0.0410 | 1.045 | ± 0.0488 | 0.437 | ± 0.0350 |
| Peonidin-malonylglucoside | 0.004 | ± 0.0003 | 0.063 | ± 0.0050 | 0.049 | ± 0.0028 | 0.007 | ± 0.0004 | 0.278 | ± 0.0256 | 0.732 | ± 0.0393 | 0.726 | ± 0.0246 | 0.258 | ± 0.0137 |
| Peonidin-dimalonylglucoside | 0.002 | ± 0.0001 | 0.016 | ± 0.0008 | 0.080 | ± 0.0035 | 0.012 | ± 0.0011 | 0.693 | ± 0.0310 | 1.356 | ± 0.0363 | 1.299 | ± 0.0664 | 0.241 | ± 0.0283 |
| Delphinidin-glucoside | 0.007 | ± 0.0003 | 0.027 | ± 0.0012 | 0.033 | ± 0.0020 | 0.019 | ± 0.0011 | nd | | 0.378 | ± 0.0303 | 0.442 | ± 0.0118 | 0.099 | ± 0.0117 |
| Delphinidin-malonylglucoside | 0.051 | ± 0.0025 | 0.216 | ± 0.0068 | 0.293 | ± 0.0151 | 0.161 | ± 0.0030 | 0.566 | ± 0.0202 | 1.916 | ± 0.0336 | 1.666 | ± 0.0537 | 0.885 | ± 0.0446 |
| Delphinidin-dimalonylglucoside | nd | | 0.064 | ± 0.0029 | 0.102 | ± 0.0035 | 0.045 | ± 0.0007 | 0.395 | ± 0.0434 | 1.362 | ± 0.0439 | 1.301 | ± 0.0372 | 0.107 | ± 0.0158 |
| Delphinidin-rutinisode | nd | | 0.009 | ± 0.0003 | 0.008 | ± 0.0002 | 0.004 | ± 0.0003 | nd | | nd | | nd | | nd | |
| Petunidin-malonylglucoside | 0.003 | ± 0.0001 | 0.038 | ± 0.0017 | 0.040 | ± 0.0018 | 0.016 | ± 0.0008 | nd | | 0.148 | ± 0.0060 | 0.127 | ± 0.0071 | 0.051 | ± 0.0016 |
| Petunidin-dimalonylglucoside | nd | | 0.012 | ± 0.0014 | 0.013 | ± 0.0008 | 0.004 | ± 0.0001 | 0.133 | ± 0.0028 | 0.399 | ± 0.0231 | 0.373 | ± 0.0293 | 0.052 | ± 0.0022 |
| Petunidin-rutinoside | nd | | 0.004 | ± 0.0002 | 0.003 | ± 0.0001 | 0.002 | ± 0.0001 | 0.029 | ± 0.0008 | 0.024 | ± 0.0009 | 0.035 | ± 0.0017 | 0.020 | ± 0.0012 |
| Petunidin-hexoside-hexoside | nd | | nd | | nd | | nd | | 0.027 | ± 0.0026 | 0.051 | ± 0.0006 | 0.045 | ± 0.0030 | 0.015 | ± 0.0006 |
| Malvidin-malonylglucoside | 0.001 | ± 0.0001 | 0.004 | ± 0.0003 | 0.007 | ± 0.0001 | 0.002 | ± 0.0001 | 0.075 | ± 0.0021 | 0.412 | ± 0.0197 | 0.364 | ± 0.0241 | 0.059 | ± 0.0015 |
| Malvidin-dimalonylglucoside | nd | | nd | | nd | | nd | | nd | | 0.245 | ± 0.0191 | 0.136 | ± 0.0123 | 0.029 | ± 0.0032 |
| Malvidin-hexoside-hexoside | nd | | nd | | nd | | nd | | 0.019 | ± 0.0020 | 0.019 | ± 0.0030 | 0.012 | ± 0.0005 | 0.011 | ± 0.0005 |
| Results are presented as the mean ± standard deviation. PM: Physiological maturity, nd: not detected. | | | | | | | | | | | | | | | | |