

Supplementary materials

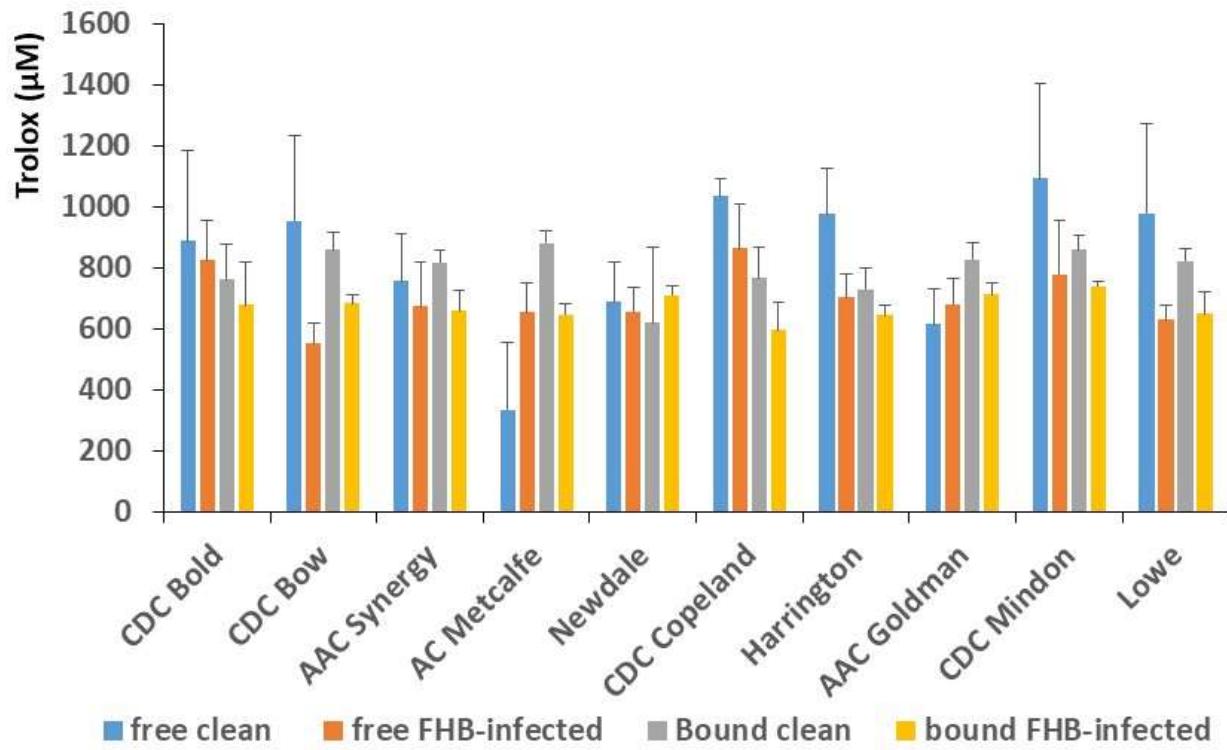
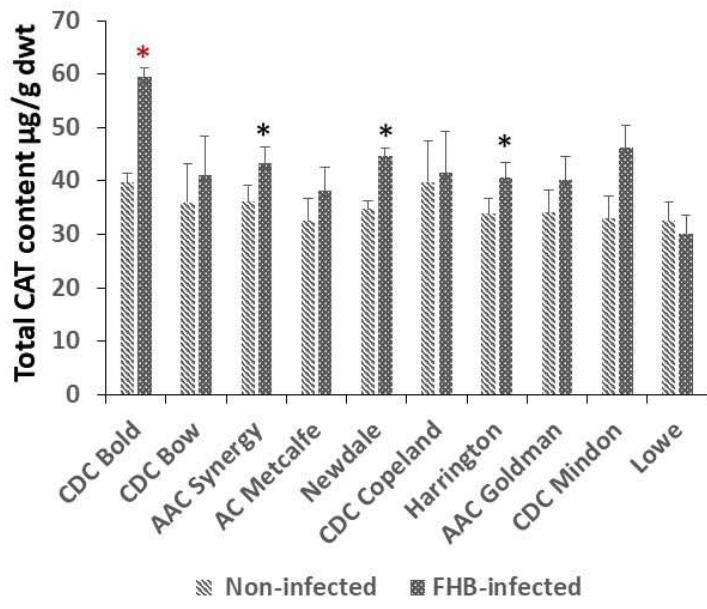


Figure S1. Antioxidant activity assay on free and bound fractions of clean and FHB-infected barley.

A.



B

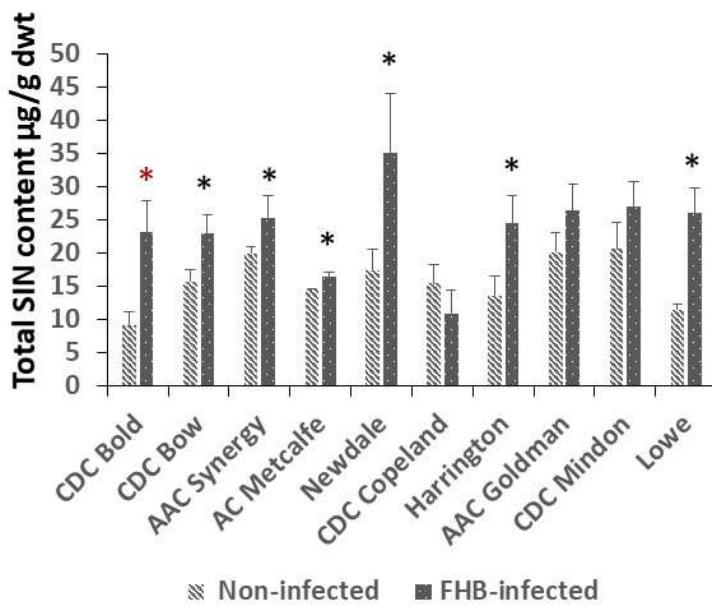
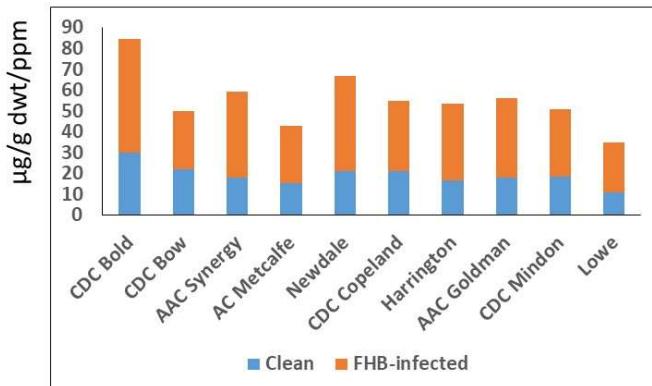


Figure S2. Changes in total (both free and bound) catechin (A) acid and sinapic acid (B) contents before and after FHB infection. *Significant at level $p \leq 0.05$ compared to the contents in non-infected (clean) grains of the tested cultivars. Susceptible check significant change is shown with *.

A



B

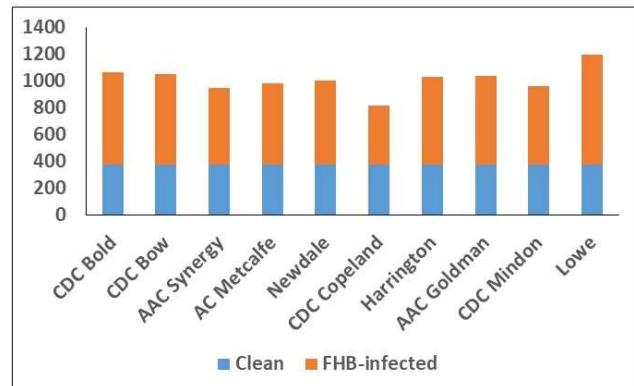
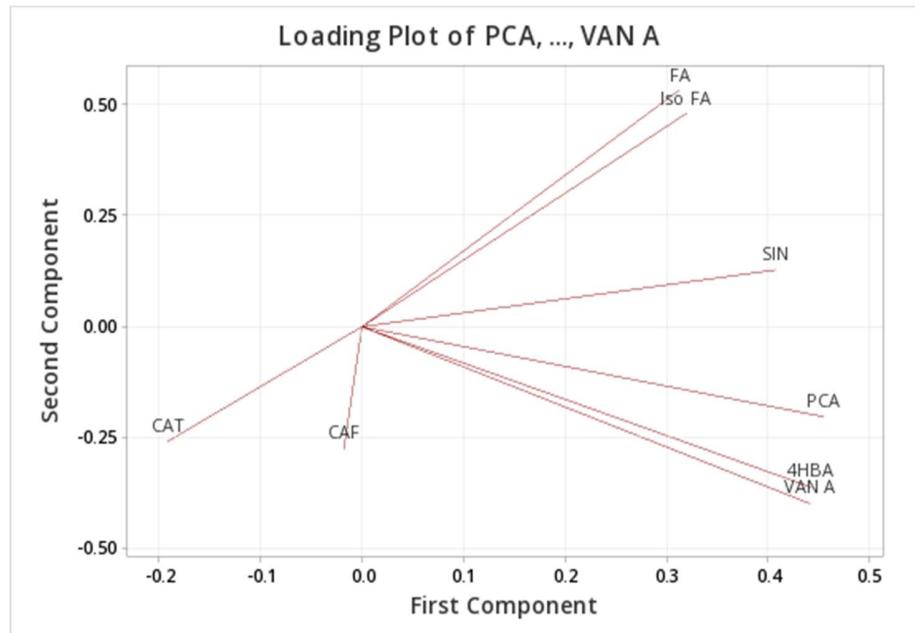


Figure S3. The sum of total individual phenolic compound contents of free (A) and bound (B) barley phenolic extracts. Blue shows clean extracts and orange shows FHB-infected barley grain extracts.

A)



B)

| Variable | PC1 | PC2 | PC3 | PC4 | PC5 |
|---------------|--------|--------|--------|--------|--------|
| PCA | 0.455 | -0.202 | -0.184 | -0.065 | 0.625 |
| CAF | -0.018 | -0.275 | 0.598 | 0.630 | 0.064 |
| SIN | 0.407 | 0.128 | -0.467 | 0.290 | -0.439 |
| FA | 0.313 | 0.532 | 0.033 | 0.031 | 0.400 |
| Iso FA | 0.320 | 0.479 | 0.242 | 0.373 | -0.129 |
| CAT | -0.192 | -0.259 | -0.533 | 0.592 | 0.243 |
| 4HBA | 0.442 | -0.360 | 0.000 | -0.077 | -0.410 |
| VAN A | 0.441 | -0.397 | 0.214 | -0.133 | 0.091 |

Figure S4. The principal component and cluster analysis of the selected phenolic compounds in tested 10 barley cultivars; (A) Loading plots of the principal component analysis; blue dots indicate each barley cultivar tested; (B) Eigenvectors for each principal component.

Table S1. The background information of cultivars used for the study

| Name | Class | Year of Registration | FHB reaction | Origin/Breeding program* | Reference |
|-----------------------|-----------------|----------------------|--------------|--------------------------|--|
| | | n | | | |
| 1. CDC Bold | General purpose | 1999 | S (check) | Canada/ U of S-CDC | CFIA (Canadian Inspection Agency) Food |
| 2. CDC Bow | Malting | 2016 | MS | Canada/ U of S-CDC | CFIA |
| 3.AAC Synergy | Malting | 2012 | I-MS | Canada/ BRDC | AAFC-Legge et al., 2014 |
| 4.AC Metcalfe | Malting | 1997 | I | Canada/ BRDC | AAFC-Legge et al., 2003 |
| 5. Newdale | Malting | 2007 | I | Canada/ BRDC | AAFC-Legge et al., 2008 |
| 6.CDC Copeland | Malting | 1999 | I | Canada/ U of S-CDC | CFIA |
| 7. Harrington | Malting | 1981 | MR | Canada/ U of S-CDC | Harvey and Rossnagel, 1984 |
| 8.AAC Goldman | Malting | 2018 | MR | Canada/ BRDC | AAFC-Legge et al., 2018 |
| 9.CDC Mindon | General purpose | 2007 | MR (check) | Canada/ U of S-CDC | Rossnagel et al, 2008 |
| 10. Lowe | Malting | 2016 | MR | Canada/ AAF-FCDC | Juskiw et al, 2019 |

* AAF-FCDC = Alberta Agriculture and Forestry - Field Crop Development Centre, Lacombe, AB; AAFC-BRDC = Agriculture and Agri-Food Canada - Brandon Research and Development Centre, Brandon, MB; and U of S - CDC = University of Saskatchewan - Crop Development Centre, Saskatoon, SK.

Table S2. Free phenolic compounds detected by high-performance liquid chromatography (HPLC) in non-infected (clean) barley cultivars.

| Cultivar | Phenolic compound ($\mu\text{g/g dwt}$) | | | |
|-----------------|---|------------|-----------|------------|
| | PCA | SIN | FA | CAT |
| CDC Bold | 0.109±0.04 | 0.36±0.1 | 2.50±0.2 | 26.9±0.9** |
| CDC Bow | ND | 0.11±0.04 | 1.79±0.2 | 20.1±5.1 |
| AAC Synergy | ND | 0.23±0.01 | 2.19±0.1 | 15.8±1.1 |
| AC Metcalfe | ND | 0.17±0.08 | 1.79±0.1 | 13.3±1.0 |
| Newdale | 0.067±0.03 | 0.15±0.01 | 2.09±0.1 | 18.7±0.8 |
| CDC Copeland | 0.056±0.02 | 0.34±0.2 | 2.48±0.2 | 18.3±0.6 |
| Harrington | ND | 0.35±0.04 | 2.78±0.1 | 13.8±1.0 |
| AAC Goldman | ND | 0.19±0.1 | 2.00±0.1 | 16.1±1.4 |
| CDC Mindon | ND | 0.42±0.2 | 2.61±0.1 | 15.5±1.0 |
| Lowe | 0.283±0.03 | 0.25±0.1 | 2.44±0.1 | 8.1±0.5* |

ND- Not detected

PCA- P coumeric acid, SIN- sinapic acid, FA- ferulic acid, CAT- catechin

**- Highest content of the specific phenolic compound

*-Lowest content of the specific phenolic compound

Table S3. Free phenolic compounds detected by HPLC in FHB-infected barley cultivars.

| Cultivar | Phenolic compound (µg/g dwt) | | | |
|-----------------|-------------------------------------|-----------|---------------|------------|
| | SIN | FA | Iso FA | CAT |
| CDC Bold | 10.8±3.6** | 2.2±0.1 | 0.36±0.1 | 41.2±5.7** |
| CDC Bow | 1.52±0.8* | 1.6±0.1 | ND | 24.9±4.2 |
| AAC Synergy | 7.58±2.8 | 2.2±0.3 | 1.96±0.5 | 29.5±3.5 |
| AC Metcalfe | 2.27±0.1* | 1.8±0.3 | 0.21±0.1 | 23.2±0.7 |
| Newdale | 12.8±6.3** | 2.3±0.2 | 1.11±0.4 | 29.6±2.1 |
| CDC Copeland | 4.76±2.0 | 1.9±0.4 | 0.63±0.2 | 26.3±3.7 |
| Harrington | 7.71±2.1 | 2.3±0.6 | 0.38±0.2 | 26.4±4.2 |
| AAC Goldman | 7.15±2.8 | 2.1±0.2 | 1.63±0.2 | 26.9±4.7 |
| CDC Mindon | 7.69±1.1 | 1.9±0.4 | 0.92±0.2 | 21.7±5.2 |
| Lowe | 7.66±1.6 | 2.4±0.2 | 0.62±0.2 | 13.2±2.8* |

ND- Not detected

SIN- sinapic acid, FA- ferulic acid, Iso-FA- Iso ferulic acid, CAT- catechin

**- Highest content of the specific phenolic compound

*- Lowest content of the specific phenolic compound

Table S4. Bound phenolic compound contents in different cultivars of non-infected (clean) barley.

| Cultivar | Phenolic compound (µg/g dwt) | | | | | | | |
|-----------------|-------------------------------------|------------|------------|-----------|---------------|------------|-------------|--------------|
| | PCA | CAF | SIN | FA | Iso FA | CAT | 4HBA | VAN A |
| CDC Bold | 140±17* | 8.6±2.6 * | 8.9±1.9* | 191±46.5* | 12.2±4.1* | 12.8±0.8* | 1.81±0.27 | 4.85±0.25* |
| CDC Bow | 228±53 | 9.9±0.7 | 15.7±1.7 | 293±41.5 | 14.2±1.8 | 15.9±2.1 | 1.88±0.07 | 6.74±1.23 |
| AAC Synergy | 214±22 | 12.8±1.0 | 19.8±0.9 | 382±14.3 | 22.5±1.0 | 20.3±2.0 | 2.90±0.32 | 9.21±1.21 |
| AC Metcalfe | 202±23 | 11.1±0.8 | 14.4±0.1 | 338±15.4 | 20.9±1.3 | 19.2±3.3 | 2.81±0.09 | 9.88±1.71** |
| Newdale | 262±45 | 11.7±1.4 | 17.4±3.0 | 359±47.7 | 18.9±3.5 | 16.1±3.7 | 2.81±1.01 | 9.25±0.34 |
| CDC Copeland | 236±34 | 10.6±2.1 | 15.2±2.5 | 342±4.2 | 16.9±2.9 | 21.5±7.1 | 1.64±0.24* | 8.19±1.49 |
| Harrington | 209±27 | 13.5±2.1 | 13.3±2.9 | 469±101** | 24.2±7.0** | 20.2±1.8 | 1.88±0.13 | 8.41±0.08 |
| AAC Goldman | 245±54 | 14.5±0.8 | 20.0±2.9** | 377±33.2 | 21.8±1.4 | 18.0±2.9 | 3.18±0.12** | 9.33±1.41 |
| CDC Mindon | 265±35 | 15.8±3.3** | 20.3±3.7** | 375±51.5 | 22.5±5.5 | 17.5±3.0 | 2.33±0.1 | 9.37±1.65** |
| Lowe | 331±96** | 10.4±1.1 | 11.3±0.8 | 368±25.5 | 17.4±1.5 | 24.6±2.9** | 2.21±0.25 | 9.41±1.45 |

Table S5. Bound phenolic compound contents in different cultivars of FHB-infected barley.

| Cultivar | Phenolic compound (µg/g dwt) | | | | | | | |
|--------------|------------------------------|------------|------------|------------|------------|------------|-------------|-------------|
| | PCA | CAF | SIN | FA | Iso FA | CAT | 4HBA | VAN A |
| CDC Bold | 305±38 | 11.0±1.3 | 12.5±1.1* | 317±54.3 | 14.6±2.7 | 18.3±3.3 | 2.63±0.36 | 9.12±1.70 |
| CDC Bow | 308±80 | 8.7±1.4 | 21.4±2.1 | 293±59.5 | 13.9±1.4* | 16.2±1.6 | 2.34±0.42 | 8.82±0.42 |
| AAC Synergy | 206±22 | 10.6±1.6 | 17.8±0.6 | 293±72.0 | 16.6±2.7 | 13.8±1.3 | 2.35±0.36 | 8.93±0.91 |
| AC Metcalfe | 238±9 | 11.3±0.5 | 14.2±0.6 | 300±51.7 | 15.2±0.7 | 15.0±1.7 | 2.35±0.13 | 9.69±1.29 |
| Newdale | 261±42 | 9.2±0.5 | 22.4±2.6** | 288±48.8 | 14.2±3.2 | 15.1±1.9 | 3.68±0.77** | 9.65±0.20 |
| CDC Copeland | 152±31* | 10.5±1.2 | 10.2±1.5 | 228±28.0* | 11.4±1.7* | 15.3±0.4 | 2.51±0.71 | 8.21±2.51 |
| Harrington | 177±43 | 8.4±2.2* | 16.8±2.2 | 412±84.6 | 19.0±8.9** | 14.3±2.3 | 1.61±0.13* | 7.20±1.62* |
| AAC Goldman | 263±21 | 10.3±1.2 | 19.3±1.3 | 322±16.4 | 18.0±3.3 | 13.4±0.9* | 3.07±0.32 | 9.51±0.98 |
| CDC Mindon | 208±50 | 12.2±1.9** | 19.4±2.6 | 304±53.5 | 18.3±4.2 | 14.6±1.0 | 2.41±0.36 | 8.12±1.98 |
| Lowe | 325±67** | 10.6±1.0 | 18.4±2.2 | 417±73.5** | 19.9±4.7** | 16.9±0.6** | 3.43±1.18 | 10.1±0.91** |