

Supplemental Table S1 Temperature of two growing seasons in Xiangshui county (119°29' E, 33°56' N, Jiangsu, China)

| Growing season | Month | Average high temperature | Average low temperature | Extreme heat | Extreme low temperature |
|------------------------------|-----------|--------------------------|-------------------------|--------------|-------------------------|
| Winter-spring growing season | January | 7°C | -3°C | 16°C | -12°C |
| | February | 11°C | 1°C | 17°C | -4°C |
| | March | 13°C | 4°C | 22°C | -2°C |
| | April | 19°C | 9°C | 24°C | 3°C |
| Summer-autumn growing season | July | 31°C | 23°C | 35°C | 21°C |
| | August | 29°C | 23°C | 32°C | 20°C |
| | September | 27°C | 31°C | 31°C | 16°C |
| | October | 21°C | 13°C | 32°C | 6°C |

Note: temperature data from the website (<https://www.tianqi24.com/xiangshui/history202107.html>).

Supplemental Table S2 Linear regression data for ferulic acid, catechin, quercetin, caffeic acid, chlorogenic acid, rutin, and glucoraphanin in broccoli head samples.

| Compounds | Regression equation | R ² |
|------------------|---------------------|----------------|
| Ferulic acid | Y=8.2453x-25.526 | 0.9998 |
| Catechin | Y=1.7503x-8.2948 | 0.9999 |
| Quercetin | Y=3.9828x-10.581 | 0.9999 |
| Caffeic acid | Y=9.207x-5.8537 | 0.9994 |
| Chlorogenic acid | Y=4.952x-64.614 | 0.9981 |
| Rutin | Y=2.1049x+16.626 | 0.9977 |
| Glucoraphanin | Y=3.5773x-11.947 | 0.9999 |

Supplemental Table S3 Condition parameters of mass spectrum analysis

| Compound | Retention time (min) | Parent ion (m/z) | Daughter ion (m/z) | Fragmentor voltage (v) | Collision energy (eV) |
|----------------------------|-------------------------|---------------------|-----------------------|---------------------------|--------------------------|
| Ergosterol | 13.827 | 379.4 | 125.0 | 125 | 10 |
| | | | 69.0 | 125 | 25 |
| Brassicasterol | 17.421 | 381.4 | 147.0 | 115 | 25 |
| | | | 69.0 | 115 | 35 |
| Cholesterol | 17.785 | 369.3 | 161.3 | 100 | 32 |
| | | | 147.2 | 100 | 33 |
| Campasterol | 21.978 | 383.4 | 161.1 | 130 | 20 |
| | | | 95.1 | 130 | 40 |
| Lanosterin | 22.044 | 409.4 | 149.0 | 120 | 25 |
| | | | 109.0 | 120 | 30 |
| Stigmasterol | 22.817 | 395.5 | 147.3 | 100 | 25 |
| | | | 83.1 | 100 | 20 |
| Beta-sitosterol | 27.347 | 397.5 | 161.0 | 100 | 25 |
| | | | 135.1 | 100 | 25 |
| Beta-sitosteryl acetate | 32.678 | 399.5 | 137.3 | 110 | 25 |
| | | | 95.3 | 110 | 25 |

Supplemental Table S4 Comparison of mineral content of broccoli heads with different growing seasons and organ sizes.

| | W15 | S15 | S11 |
|--|---------------------|----------------------|-----------------------|
| phosphorus ($\mu\text{g/g}$) | 8761 \pm 359.43 | 9529.40 \pm 252.74 | 10207.80 \pm 705.70 |
| zinc ($\mu\text{g/g}$) | 8.50 \pm 2.17 | 8.20 \pm 2.28 | 5.00 \pm 0.71 |
| potassium ($\mu\text{g/g}$) | 2284.50 \pm 52.92 | 2261.00 \pm 87.39 | 2230.20 \pm 162.93 |
| sodium ($\mu\text{g/g}$) | 76.50 \pm 6.77 | 74.00 \pm 10.51 | 68.00 \pm 5.15 |
| magnesium ($\mu\text{g/g}$) | 155.67 \pm 11.96 | 166.00 \pm 6.40 | 167.20 \pm 6.87 |
| calcium ($\mu\text{g/g}$) | 326.00 \pm 75.48 | 256.80 \pm 12.32 | 286.80 \pm 10.33 |
| iron ($\mu\text{g/g}$) | 119.50 \pm 19.55 | 326.80 \pm 129.88 | 120.40 \pm 5.03 |

Notes: the mean \pm SEM are shown. Number of replicates $n = 6\text{-}8$.

Supplemental Table S5 The principal component analysis (PCA) of individual phenolic compound and calculation of comprehensive scores in the three groups.

| Samples | Comprehensive average scores |
|---------|------------------------------|
| S11 | 0.0433 |
| S15 | 0.0067 |
| W15 | -0.0500 |

Supplemental Table S6 The PCA of 6 phytosterol contents and calculation of comprehensive scores in the three groups (W15, S15, and S11).

| Samples | Comprehensive average scores |
|---------|------------------------------|
| S11 | 0.0475 |
| S15 | 0.0410 |
| W15 | -0.0780 |

Supplemental Table S7 The PCA of the mineral contents and calculation of comprehensive scores in the three groups (W15, S15, and S11).

| Samples | Comprehensive average scores |
|---------|------------------------------|
| S15 | 0.0220 |
| W15 | 0.0083 |
| S11 | 0.0340 |