SUPPLEMENTARY MATERIAL

Authentication of Greek PDO Kalamata table olives: a novel non-target HRMS approach

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Table S1. Target list of phenolic compounds.

| Compound Class | Compound | Molecular formula | [M-H]⁻ (m/z) (min) | tR (min) | Fragments (m/z) | Fragment elemental formula |
|----------------|----------|------------------|--------------------|---------|----------------|--------------------------|
| flavonoids     |         |                  |                    |         |                |                          |
| Apigenin       | C_{15}H_{10}O_{5} | 269.0455          | 8.10               |         | 117.0340       | C_{8}H_{4}O_{2}           |
|               |          |                  |                    |         | 151.0031       | C_{14}H_{9}O_{4}          |
|               |          |                  |                    |         | 245.0819       | C_{13}H_{7}O_{4}          |
|               |          |                  |                    |         | 123.0452       | C_{12}H_{4}O_{2}          |
|               |          |                  |                    |         | 203.0714       | C_{12}H_{4}O_{1}          |
| Epicatechin    | C_{15}H_{10}O_{6} | 289.0718          | 4.30               |         | 113.0295       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 151.0037       | C_{7}H_{3}O_{2}           |
|               |          |                  |                    |         | 175.0401       | C_{10}H_{10}O_{1}         |
| Luteolin       | C_{15}H_{10}O_{6} | 285.0405          | 7.30               |         | 133.0446       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 134.0346       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 203.0819       | C_{10}H_{10}O_{1}         |
| phenolic acids |         |                  |                    |         |                |                          |
| Caffeic acid   | C_{9}H_{8}O_{4} | 179.035           | 1.40               |         | 125.0244       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 134.0346       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 97.0295        | C_{6}H_{3}O_{2}           |
| Ferulic acid   | C_{10}H_{10}O_{4} | 193.0506          | 3.00               |         | 122.0373       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 137.0608       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 154.0272       | C_{9}H_{4}O_{2}           |
| Gallic acid    | C_{7}H_{6}O_{3} | 169.0142          | 1.30               |         | 123.008        | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 166.9976       | C_{8}H_{5}O_{2}           |
| p-coumaric acid| C_{9}H_{9}O_{3} | 163.0401          | 2.60               |         | 119.0502       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 93.0344        | C_{7}H_{4}O_{2}           |
| Syringic acid  | C_{9}H_{10}O_{5} | 197.0455          | 1.40               |         | 123.008        | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 166.9976       | C_{8}H_{5}O_{2}           |
| Homovanillic acid | C_{9}H_{10}O_{4} | 181.0491          | 1.48               |         | 122.0373       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 137.0608       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 154.0272       | C_{9}H_{4}O_{2}           |
| Hydroxytyrosol | C_{8}H_{10}O_{3} | 153.0557          | 3.50               |         | 123.0451       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 95.0502        | C_{8}H_{4}O_{2}           |
| Tyrosol        | C_{8}H_{10}O_{2} | 137.0608          | 4.10               |         | 119.0495       | C_{8}H_{4}O_{2}           |
|               |          |                  |                    |         | 107.0496       | C_{8}H_{4}O_{2}           |
|               |          |                  |                    |         | 93.0344        | C_{7}H_{4}O_{2}           |
| Vanillin       | C_{8}H_{9}O_{3} | 151.0401          | 4.70               |         | 136.0158       | C_{7}H_{4}O_{2}           |
|               |          |                  |                    |         | 108.0217       | C_{7}H_{4}O_{2}           |
|               |          |                  |                    |         | 92.0268        | C_{8}H_{4}O_{2}           |
| lignans        | Pinoresinol | C_{20}H_{22}O_{6} | 357.1344           | 6.49    | 151.0401       | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 136.0166       | C_{8}H_{5}O_{2}           |
| secoridoids    | Oleuropein  | C_{25}H_{32}O_{13}| 539.1722           | 5.96    | 89.0244        | C_{8}H_{5}O_{2}           |
|               |          |                  |                    |         | 275.0925       | C_{15}H_{14}O_{4}         |
|               |          |                  |                    |         | 307.0823       | C_{15}H_{14}O_{7}         |
Table S2. Evaluation of scaling methods used by PLS-DA model.

| Method               | $R^2_X$ | $R^2_Y$ | $Q^2$ | RMSEE | RMSEP | Classification Total Accuracy | Score  |
|----------------------|---------|---------|-------|-------|-------|-------------------------------|--------|
| Mean Centering       | 0.867   | 0.971   | 0.966 | 0.0711| 0.0921| 1.00 1.00 1.00 | 0.931  |
| Autoscaling          | 0.676   | 0.988   | 0.979 | 0.0528| 0.0830| 1.00 1.00 1.00 | 0.913  |
| Range scaling        | 0.739   | 0.991   | 0.984 | 0.0466| 0.0805| 1.00 1.00 1.00 | 0.925  |
| Pareto scaling       | 0.815   | 0.981   | 0.975 | 0.0674| 0.0745| 1.00 1.00 1.00 | **0.932** |
| Vast                 | 0.555   | 0.987   | 0.955 | 0.0563| 0.0992| 1.00 1.00 1.00 | 0.884  |
| Level                | 0.736   | 0.989   | 0.976 | 0.0519| 0.0776| 1.00 1.00 1.00 | 0.923  |
| Mean Centering Log2  | 0.972   | 0.978   | 0.971 | 0.0727| 0.4880| 1.00 0.215 0.831 | 0.810  |
| VSN                  | 0.931   | 0.034   | 0.0360| 0.4701| 0.5020| 0.412 0.215 0.369 | 0.397  |
| PQN                  | 0.922   | 0.942   | 0.914 | 0.0745| 0.0859| 1.00 1.00 1.00 | 0.925  |
Figure S1. (a) EIC Chromatograms of the two mass features (±5 mDa); (b) Centroid mode spectra for the tR of 3.53 min; (c) MS/MS spectra of hydroxytyrosol (m/z 153.0558) eluting as same retention time as m/z 123.0452.