

# Targeted UHPLC-HRMS (Orbitrap) Polyphenolic and Capsaicinoid Profiling for the Chemometric Characterization and Classification of Paprika with Protected Designation of Origin (PDO) Attributes

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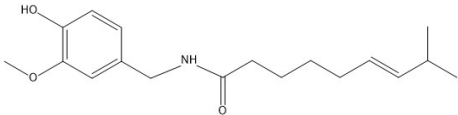
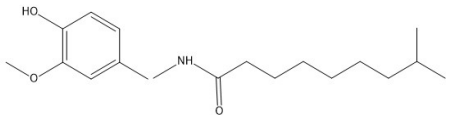
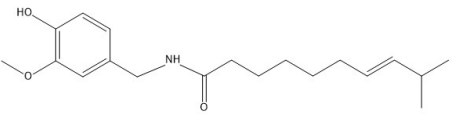
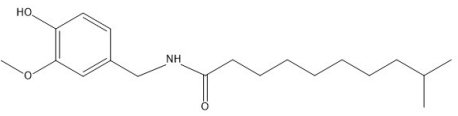
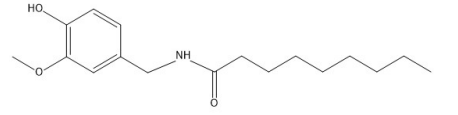
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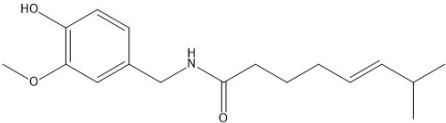
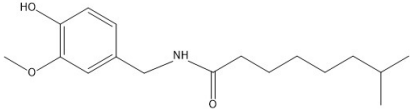
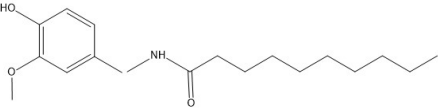
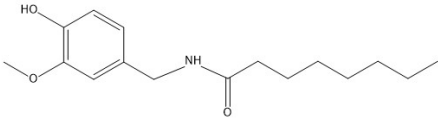
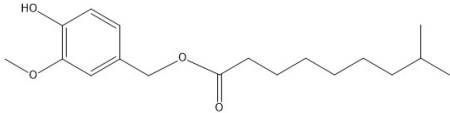
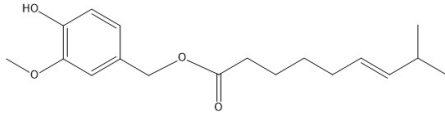
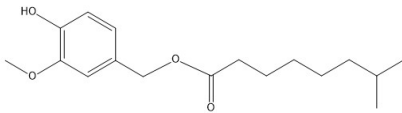
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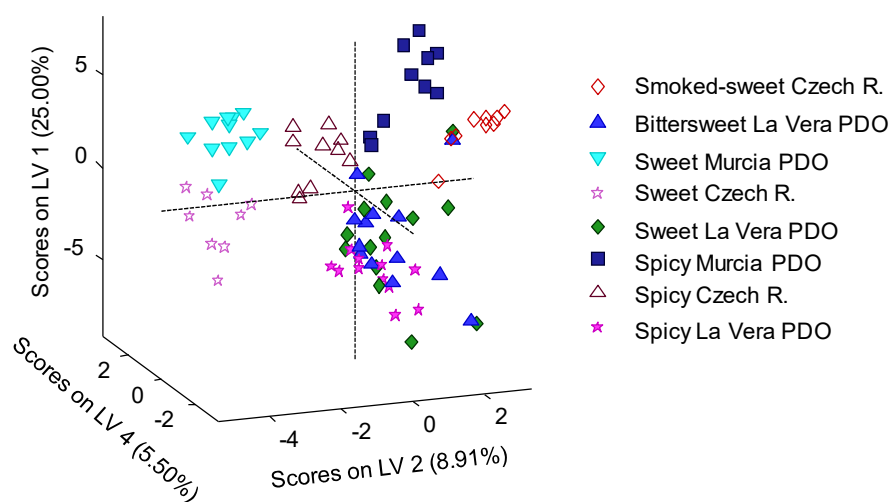
**Table 1.** Chemical structures of the studied capsaicinoids and capsinoids.

| Compounds            | Formula                                         | CAS number | Structure                                                                            |
|----------------------|-------------------------------------------------|------------|--------------------------------------------------------------------------------------|
| <i>Capsaicinoids</i> |                                                 |            |                                                                                      |
| Capsaicin            | C <sub>18</sub> H <sub>27</sub> NO <sub>3</sub> | 404-86-4   |  |
| Dihydrocapsaicin     | C <sub>18</sub> H <sub>29</sub> NO <sub>3</sub> | 19408-84-5 |  |
| Homocapsaicin        | C <sub>19</sub> H <sub>29</sub> NO <sub>3</sub> | 58493-48-4 |  |
| Homodihydrocapsaicin | C <sub>19</sub> H <sub>31</sub> NO <sub>3</sub> | 20279-06-5 |  |
| Nonivamide           | C <sub>17</sub> H <sub>27</sub> NO <sub>3</sub> | 2444-46-4  |  |

|                       |                                                 |             |                                                                                      |
|-----------------------|-------------------------------------------------|-------------|--------------------------------------------------------------------------------------|
| Norcapsaicin          | C <sub>17</sub> H <sub>25</sub> NO <sub>3</sub> | 61229-08-1  |    |
| Nordihydrocapsaicin   | C <sub>17</sub> H <sub>27</sub> NO <sub>3</sub> | 28789-35-7  |    |
| N-vanillyl decanamide | C <sub>18</sub> H <sub>29</sub> NO <sub>3</sub> | 31078-36-1  |    |
| N-vanillyl octanamide | C <sub>16</sub> H <sub>25</sub> NO <sub>3</sub> | 58493-47-3  |    |
| <b>Capsinoids</b>     |                                                 |             |                                                                                      |
| Dihydrocapsiate       | C <sub>18</sub> H <sub>28</sub> O <sub>4</sub>  | 205687-03-2 |   |
| Capsiate              | C <sub>18</sub> H <sub>26</sub> O <sub>4</sub>  | 205687-01-0 |  |
| Nordihydrocapsiate    | C <sub>17</sub> H <sub>26</sub> O <sub>4</sub>  | 220012-53-3 |  |

**Table 2.** HRMS spectral data of the studied Capsaicinoids and Capsinoids.

| Compounds            | Chemical formula                                | HRMS spectrum                                 |                                                 |                                 |
|----------------------|-------------------------------------------------|-----------------------------------------------|-------------------------------------------------|---------------------------------|
|                      |                                                 | [M-H] <sup>+</sup> m/z<br>calculated<br>value | [M-H] <sup>+</sup> m/z<br>experimental<br>value | Accurate<br>mass error<br>(ppm) |
| <i>Capsaicinoids</i> |                                                 |                                               |                                                 |                                 |
| Capsaicin            | C <sub>18</sub> H <sub>27</sub> NO <sub>3</sub> | 304.1918                                      | 304.1912                                        | -1.972                          |
| Dihydrocapsaicin     | C <sub>18</sub> H <sub>29</sub> NO <sub>3</sub> | 306.2075                                      | 306.2068                                        | -2.286                          |
| Homocapsaicin        | C <sub>19</sub> H <sub>29</sub> NO <sub>3</sub> | 318.2075                                      | 318.2069                                        | -1.886                          |
| Homodihydrocapsaicin | C <sub>19</sub> H <sub>31</sub> NO <sub>3</sub> | 320.2231                                      | 320.2227                                        | -1.249                          |
| Nonivamide           | C <sub>17</sub> H <sub>27</sub> NO <sub>3</sub> | 292.1918                                      | 292.1913                                        | -1.711                          |
| Norcapsaicin         | C <sub>17</sub> H <sub>25</sub> NO <sub>3</sub> | 290.1762                                      | 290.1755                                        | -2.412                          |
| Nordihydrocapsaicin  | C <sub>17</sub> H <sub>27</sub> NO <sub>3</sub> | 292.1918                                      | 292.1913                                        | -1.711                          |
| N-vanilly decanamide | C <sub>18</sub> H <sub>29</sub> NO <sub>3</sub> | 306.2075                                      | 306.2068                                        | -2.286                          |
| N-vanilly octanamide | C <sub>16</sub> H <sub>25</sub> NO <sub>3</sub> | 278.1762                                      | 278.1755                                        | -2.516                          |
| <i>Capsinoids</i>    |                                                 |                                               |                                                 |                                 |
| Dihydrocapsiate      | C <sub>18</sub> H <sub>28</sub> O <sub>4</sub>  | 307.1915                                      | 307.1907                                        | -2.6042                         |
| Capsiate             | C <sub>18</sub> H <sub>26</sub> O <sub>4</sub>  | 305.1758                                      | 305.1751                                        | -2.2938                         |
| Nordihydrocapsiate   | C <sub>17</sub> H <sub>26</sub> O <sub>4</sub>  | 293.1758                                      | 293.175                                         | -2.7287                         |



**Figure 1.** 3D plot of scores of PLS-DA model (LV1 vs. LV2 vs. LV3) when UHPLC-HRMS polyphenolic profiles were employed as chemical descriptors of the analyzed paprika samples according to their production regions and flavor varieties.