

# Supplementary material

## **Silage Fermentation: A Potential Biological Approach for the Long-term Preservation and Recycling of Polyphenols and Terpenes in Globe Artichoke (*Cynara scolymus* L.) By-products**

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**Table SM 1:** The limit of detection ( LOD) and limit of quantification ( LOQ) and linear equation of polyphenols

| Standard                      | Standard curve       | R <sup>2</sup> | Linear range<br>(µg/L) | LOD<br>(µg/L) | LOQ<br>(µg/L) |
|-------------------------------|----------------------|----------------|------------------------|---------------|---------------|
| Salicylic acid                | y=293.255x-287.844   | 0.9994         | 10-500                 | 1.68          | 5.60          |
| Caffeic acid                  | y=52.8777x+2122.5    | 0.9997         | 58.5-11700             | 4.26          | 14.21         |
| Vanillic acid                 | y=2.81622x-29.6034   | 0.9997         | 50-1000                | 14.01         | 46.70         |
| Ferulic acid                  | y=10.5697x-86.114    | 0.9993         | 20-1000                | 5.65          | 18.83         |
| Luteolin                      | y=3.18188x+1874.48   | 0.9993         | 500-10000              | 10.22         | 34.07         |
| Chlorogenic acid              | y=20.4979x+732.94    | 0.9999         | 200-10000              | 12.94         | 43.13         |
| Syringic acid                 | y=4.74307x-37.5689   | 0.9993         | 21.6-2160              | 6.09          | 20.30         |
| Cynarin                       | y=8.50171x+42.9748   | 0.9997         | 20-10000               | 6.40          | 21.34         |
| Gallic acid                   | y=13.865x-197.859    | 0.9991         | 50-5000                | 14.41         | 48.03         |
| Apigenin                      | y=0.048618x-0.904486 | 0.9997         | 500-10000              | 2.92          | 9.74          |
| Protocatechuic acid           | y=68.4094x-338.16    | 0.9993         | 50-2500                | 4.12          | 13.73         |
| <i>p</i> -Coumaric acid       | y=93.4543x-63.5635   | 0.9992         | 50-2500                | 3.72          | 12.40         |
| Phlorizin                     | y=26.1328x-586.255   | 0.9995         | 50-2500                | 2.96          | 9.87          |
| <i>p</i> -Hydroxybenzoic acid | y=95.7398x-179.144   | 0.9998         | 20-1000                | 3.71          | 12.38         |
| (-)-Epicatechin gallate       | y=8.08908x+0.641407  | 0.9998         | 20-500                 | 4.96          | 16.54         |

**Table SM 2 :** Characteristic ions of polyphenols

| Compounds                         | [M – H] <sup>-</sup><br>m/z | HPLC-ESI(-)-MS <sup>2</sup> expt<br>m/z (% base peak)          | Reference |
|-----------------------------------|-----------------------------|----------------------------------------------------------------|-----------|
| 1- <i>O</i> -caffeoylquinic acid  | 353                         | MS <sup>2</sup> [353]: 191 (100), 197 (5)                      | [1]       |
| 4- <i>O</i> -caffeoylquinic acid  | 353                         | MS <sup>2</sup> [353]: 173 (100), 179 (53), 191 (16), 135 (12) |           |
| Apigenin 7- <i>O</i> -glucuronide | 445                         | MS <sup>2</sup> [445]: 269 (100), 175 (20)                     |           |

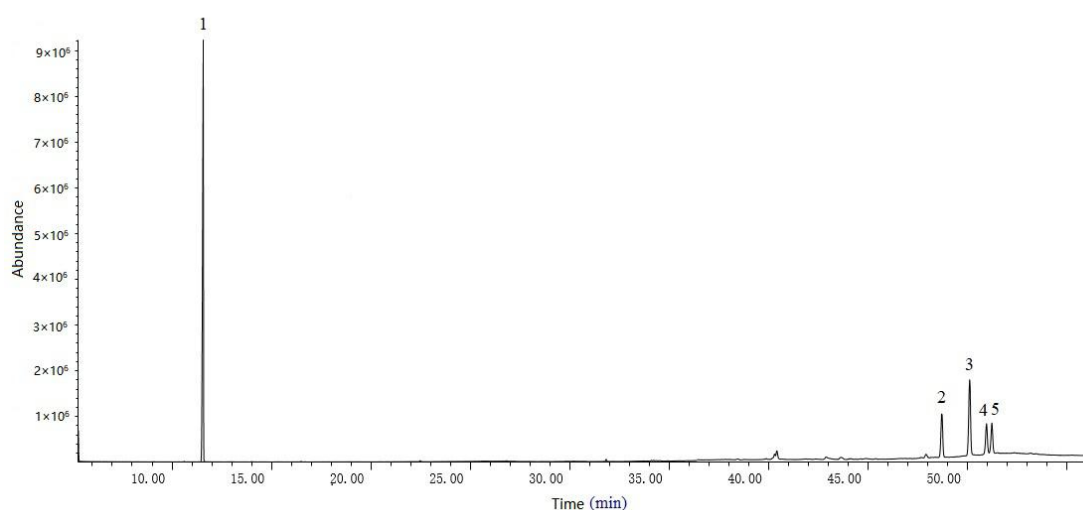
**Table SM 3:** Electron Impact Mass Spectra (EI-MS) of the sesquiterpene lactones and the pentacyclic triterpenes identified in the form of TMS derivatives

| Compounds                           | Fragment ions of EI-MS (70 eV), m/z                                           | Reference |
|-------------------------------------|-------------------------------------------------------------------------------|-----------|
| $\Psi$ -Taraxasterol-TMS derivative | 498[M] <sup>+</sup> (6), 483(2), 408(12), 218(10), 203(16), 189(100), 175(19) | [2]       |
| Taraxasterol-TMS derivative         | 498[M] <sup>+</sup> (8), 483(3), 408(8), 218(9), 203(21), 189(100), 175(21)   |           |

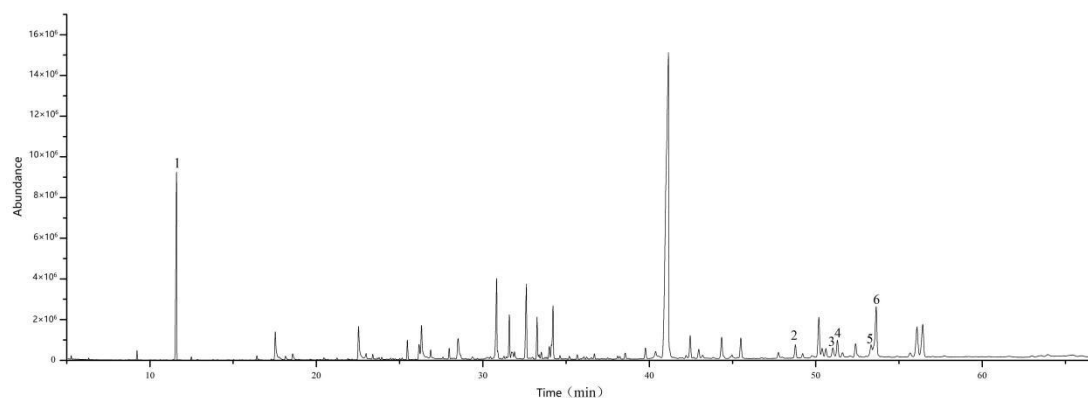
**Table SM 4:** Identification of terpenoids in the fat soluble extract of artichoke

| RT /min                        | Compound             | RI     | RI <sub>ref</sub> | Qualitative methods |
|--------------------------------|----------------------|--------|-------------------|---------------------|
| <b>Pentacyclic triterpenes</b> |                      |        |                   |                     |
| 51.024                         | $\alpha$ -Amyrin     | 3385.0 | 3379.3            | A/B                 |
| 51.293                         | Lupeol               | 3396.1 | 3390.8            | A/B                 |
| 53.325                         | $\Psi$ -Taraxasterol | 3480.5 | -                 | C [2,3]             |
| 53.623                         | Taraxasterol         | 3493.2 | -                 | C [2,3]             |
| <b>Sterols</b>                 |                      |        |                   |                     |
| 48.775                         | Stigmasterol         | 3290.3 | 3285.6            | A/B                 |
| 50.188                         | $\beta$ -Sitosterol  | 3349.1 | 3344              | A/B                 |

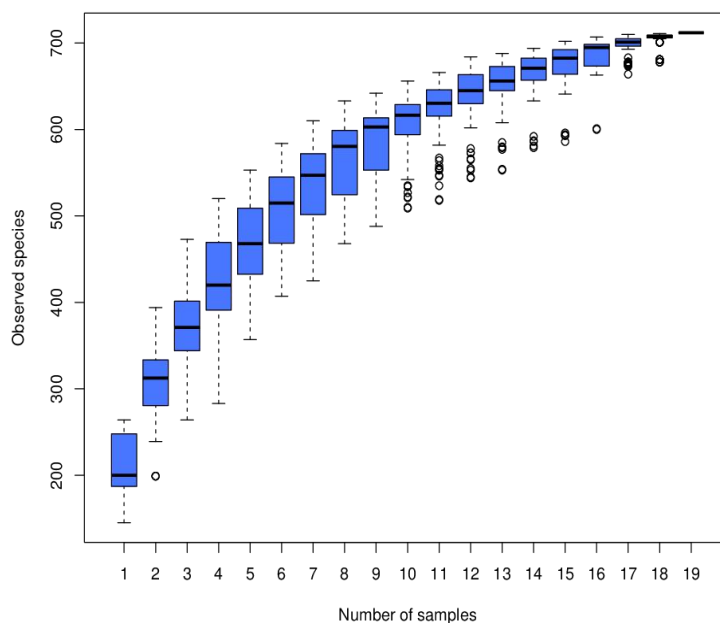
RT: retention time; RI: retention index; RI<sub>ref</sub>: retention index in reference; A: Qualitative by National Institute of Standard and Technology (NIST) mass spectral library; B: Qualitative by standard sample; C: Qualitative analysis by mass spectrometry information in reference.



**Fig SM 1.** Total ion efflux of terpene standards. 1. N-hexadecane; 2. Stigmasterol; 3.  $\beta$ -sitosterol; 4.  $\alpha$ -Amyrin; 5. Lupeol.



**Fig SM 2.** Total ion outflow of terpenoids from artichoke by-product. 1. N-hexadecane; 2. Stigmasterol; 3.  $\beta$ -sitosterol; 4.  $\alpha$ -Amyrin; 5.  $\Psi$ -Taraxasterol; 6. Taraxasterol



**Fig SM 3.** Species accumulation boxplot.

## References:

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