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# Influence of Encapsulation Parameters on the Retention of Polyphenols in Blackthorn Flower Extract

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**Abstract:** In order to utilize the benefits of blackthorn flower polyphenols and provide their stabilization during processing and storage, and to facilitate their application in functional food products, this study aimed to evaluate the encapsulation parameters during the spray-drying process of blackthorn flower extract. The effect of the type of wall material (maltodextrin (MD) and its mixtures with gum arabic (GA) and inulin (IN)), its ratio to extract dry matter (0.5, 1, and 2) and drying temperature (120, 150, and 180 °C) on the concentration of different polyphenolic groups was studied. While the lowest applied amount of wall material at the lowest drying temperature enabled efficient encapsulation of all polyphenolic groups, the type of wall material applied caused significant differences in retention. The highest concentrations of both phenolic acids and flavonoids were achieved with the addition of 25% of GA in MD. Unlike the addition of GA, mixtures of MD with IN did not show a positive effect on the retention of polyphenols. Selected encapsulation parameters ensured the high retention of total phenolics, namely 87.87% of the content determined in the liquid extract prior to spray drying, thereby providing a polyphenol-rich product with great potential for application in functional food and the nutraceutical industry.

**Keywords:** blackthorn flowers; spray-drying; wall material; UPLC-MS/MS; polyphenols



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## 1. Introduction

Blackthorn (*Prunus spinosa* L.) is a medicinal wild species of the genus *Prunus*, all of whose parts (fruits, flowers, leaves, branches, bark, and roots) have been used for centuries in traditional medicine due to their health benefits, mainly attributed to phytochemicals [1–3]. Scientific research has been focused mostly on the identification and determination of bioactive compounds in blackthorn fruits and leaves, while only a few studies have included blackthorn flowers. Polyphenols represent a significant class of bioactive compounds in blackthorn flowers [4–12] and the most prevalent are kaempferol, quercetin, and their glycosides (mainly arabinose, xylose, and rhamnose) [9–13], type A procyanidins, and phenolic acids [9–12,14], represented mostly by *p*-hydroxybenzoic acid [15]. All these compounds are considered responsible for blackthorn's reported antioxidant, anti-inflammatory, and antitumor effects [16,17].

The stability of polyphenols is influenced by numerous factors, such as oxygen, light, humidity, temperature, and pH, exposure to which results in a decrease or even total loss of their bioactivity [18]. The most widely applied methods for their stabilization is encapsulation methods, which increase their stability, preserve bioactivity, and broaden their application potential through increased bioavailability and possibility of controlled release and delivery [19].

There are numerous encapsulation methods available; however, it is of utmost importance to carefully select the encapsulation method and appropriate parameters depending on the material characteristics and properties of the bioactive molecules.

One of the most widely applied and yet effective encapsulation methods, primarily used for heat-sensitive polyphenol-rich plant extracts, is spray drying [20]. Spray drying enables the transformation of liquid polyphenolic extracts into a more stable powdered microcapsule form. The effectiveness of the process depends upon the parameters applied, mainly the selection of the wall material, its concentration in relation to the active compound (extract), and drying temperature.

The most widely used wall materials for the spray-drying encapsulation of polyphenols are polysaccharides (maltodextrins of different dextrose equivalence) and gum arabic [21]. These wall materials can be applied separately or as mixtures, as several studies have shown that using a mixture of wall materials leads to greater stability of the polyphenols than using a single polymer [22–24].

Maltodextrins are obtained by partial acid or enzymatic hydrolysis of starches. They are relatively inexpensive, with neutral aroma and flavour and low viscosity at high dry matter concentration, and they satisfactorily stabilize polyphenols from oxidation [25,26]. The major disadvantages of maltodextrins are low emulsion capacity and limited retention of volatiles; therefore, they are widely combined with other wall materials, most commonly gums, primarily with gum arabic [27,28]. Gum arabic is an edible biopolymer of D-glucuronic acid, L-ramose, D-galactose, and L-arabinose with about 2% protein structure, and because of its low protein content has good emulsifier properties and is considered an excellent wall material for encapsulation of polyphenols. However, application of gum arabic is limited due to its high cost, availability (300 g/plant/year), and impurities [29].

Recently, new materials have been exploited as encapsulating agents, such as inulin, a low-cost dietary fiber with a prebiotic effect and without taste or odor [30–32]. Apart from its prebiotic effect, inulin is a material of choice for delivering bioactives that are susceptible to degradation in the human digestive system, as it is released only in the intestine [33].

One of the main advantages of the spray-drying encapsulation method is short exposure to elevated temperatures. Usually, applied temperatures vary in range from 150 °C to 210 °C [34]; however, for encapsulation of heat-sensitive compounds such as polyphenols, temperatures mostly do not exceed 180 °C [22,30].

Several studies of the encapsulation of polyphenols by spray drying leaf extracts have been reported, such as from Camellia sinenis [35], Satureja montana [25], guava [27], olive [30], laurel [36], nettle [37], etc., while there are few studies of polyphenols encapsulated by spray drying flower extracts [9,10,38]. To the best of our knowledge, none of the published studies have evaluated the encapsulation of blackthorn flower extract.

Therefore, this study aimed to evaluate the influence of three crucial spray-drying encapsulation parameters on the retention of polyphenols in blackthorn flower extract: wall material (maltodextrin (MD), two mixtures of maltodextrin and gum arabic (MD/GA), and two mixtures of maltodextrin and inulin (MD/IN)), wall material-to-extract dry matter ratio (0.5:1, 1:1, and 2:1 (*w*/*w*)), and drying temperature (120 °C, 150 °C, and 180 °C) on the retention of polyphenols in encapsulated blackthorn flower extract.

## 2. Materials and Methods

### *2.1. Materials*

Naturally dried blackthorn flowers (*Prunus spinosa flos*) were collected and purchased from the certified firm Suban Ltd. (Strmec, Croatia), batch number 63453.

Maltodextrin (MD) dextrose equivalent 13–17 (Sigma-Aldrich, St. Louis, MI, USA), gum arabic (GA) (Acrõs organic, Thermo Fisher Scientific, Geel, Belgium), and inulin (IN) (Dukat, Zagreb, Croatia) were used as wall materials. Methanol (J.T. Baker Inc., Phillipsburg, NY, USA), ethanol, formic acid, and acetonitrile (BDH Prolabo, VWR International, Lutterworth, England) were HPLC grade. Commercial phenol standards were used: quercetin-3-glucoside, kaempferol-3-rutinoside, caffeic acid, ferulic acid, gallic acid, chlorogenic acid, *p*-coumaric acid (Sigma-Aldrich, St. Louis, MI, USA); epicatechin, catechin, epigallocatechin gallate, epicatechin gallate, procyanidin B1, luteolin (Extrasynthese, Genay, France) and quercetin-3-rutinoside (Acrõs organic, Thermo Fisher Scientific, Geel, Belgium).

### 2.2. Preparation of Blackthorn Flower Extract

Blackthorn flower extract was obtained with a 1:7 (*w*/*v*) naturally dried blackthorn flower:distilled water ratio, stirred well and extracted in an Elmasonic S40H ultrasonic bath (Elmasonic, Singen, Germany) at a temperature of 50 °C for 20 min at an ultrasonic frequency of 37 kHz. After extraction, the resulting extracts were filtered through a filter paper into a collecting container. The total amount of primary aqueous blackthorn flower extract was about 6 L.

### 2.3. Encapsulation by Spray Drying

The obtained blackthorn extract was encapsulated using the spraydrying method on a laboratory-scale spray dryer Lab-Plant SD-60 (United Kingdom) with a co-current flow with 1 mm spray nozzle, deblocking speed at medium level, at a constant feed flow 485 mL/h and airflow 3.5 m/s, and an outlet air temperature from 60 to 80 °C. The spray-drying process was carried out according to the full factorial experimental design as follows: five different wall materials (maltodextrin (MD), maltodextrin combined with 25% and 50% (*w*/*w*) gum arabic (MD + 25%GA and MD + 50%GA, respectively), and maltodextrin combined with 25% and 50% (*w*/*w*) inulin (MD + 25%IN, and MD + 50% IN, respectively) were applied in three different wall materials to extract dry matter ratios (0.5:1, 1:1, and 2:1 (*w*/*w*)) and at three different drying temperatures (120, 150 and 180 °C).

To achieve homogeneous dispersion of the wall material in the blackthorn extract, mixtures of wall material and blackthorn flower extract according to the experimental design were homogenized using an HSC Ceramic Hot Top-Plate Stirrer (Velp, Usmate Velate, Italy) magnetic stirrer at a temperature of 50 °C for 30 min and encapsulated by spray-drying. All powders were produced in duplicate and stored in plastic containers in an inert gas atmosphere at 4 °C until analysis.

### 2.4. Determination of Polyphenols

Polyphenols were extracted from 1 g of powder with 6 mL of 80% aqueous (*v*/*v*) methanol solution (HPLC grade, J.T. Baker Inc., Phillipsburg, NY, USA) in an ultrasonic bath at a temperature of 50 °C for 15 min. The extract thus obtained was filtered through filter paper into a 10 mL graduated flask and made up to volume with 80% methanol. The obtained extracts were filtered through a 0.45 µm microfilter (Macherey-Nagel, Dueren, Germany) into vials as samples for UPLC-MS/MS analysis.

Phenolic compounds were identified and quantified by UPLC-MS/MS (ultra-performance liquid chromatography and tandem mass spectrometry) according to the method previously described by Elez Garofulić et al. [10] using an Agilent series 1290 RRLC instrument coupled with an Agilent 6430 Triple Quadrupole LC/MS mass spectrometer (Agilent, Santa Clara, CA, USA). The ionization was performed using an ESI ion source in positive and negative mode with nitrogen as a desolvation and collision gas. Drying gas temperature was set at 300 °C, flow rate at 11 L/h, nebulizer pressure at 40 psi, and capillary voltage at 4000/3500 V. A Zorbax Eclipse Plus C18 column from Agilent (100 × 2.1 mm; 1.8 µm particle size) was used for separations under the following conditions: injection volume 2.5 µm and column temperature 35 °C.

For identification and quantification of polyphenols in the blackthorn extract, commercially available standards were used: quercetin-3-glucoside, kaempferol-3-rutinoside, caffeic acid, ferulic acid, gallic acid, chlorogenic acid, *p*-coumaric acid, epicatechin, catechin, epigallocatechin gallate, epicatechin gallate, procyanidin, luteolin, and quercetin-3-rutinoside. The identification of polyphenols was carried out by comparing retention time and *m*/*z* values with corresponding standards. Compounds lacking reference standards were mass-identified according to their spectral data by comparing molecular and ion fragments with literature data. Identification pathways for those compounds have been previously reported [10], while quantification was performed as follows: neochlorogenic acid was quantified according to the chlorogenic acid calibration curve; 3-*p*-coumaroylquinic and 4-*p*-coumaroylquinic acid according to the *p*-coumaric acid calibration curve; feru-

loylquinic acid according to the ferulic acid calibration curve; kaempferol rhamnosylhexoside, pentosylhexoside, pentoside, rhamnoside and acetylhexoside according to the kaempferol-3-rutinoside calibration curve; quercetin pentosylhexoside, pentoside, rhamnoside and acetylhexoside according to the quercetin-3-glucoside calibration curve; and isorhamnetin-rutinoside according to the quercetin-3-rutinoside calibration curve.

Individual concentrations of polyphenols were summed to obtain total hydroxycinnamic acids, total hydroxybenzoic acids, total flavanols, total flavonoids, total flavons, and total phenolic content. All measurements were taken in duplicate and the results are expressed as mean value ± standard deviation in mg/100 e.d.m. (extract dry matter).

### 2.5. Experimental Design and Statistical Analysis

The experimental design and statistical analysis were performed using Statsoft STATISTICA v.12 software (Statsoft Inc., Tulsa, OK, USA). All experiments and analysis were performed in duplicate. A mixed-level full factorial design was chosen to evaluate the effect of wall material, wall material:extract dry matter ratio, and drying temperature on the concentration of individual polyphenolic classes and total polyphenols in encapsulated blackthorn flower extract. The independent variable type of the wall material was observed at 5 levels, while the wall material:extract dry matter ratio and drying temperature were observed at 3 levels, thereby providing a total of 45 experimental trials. The normality and homoscedasticity of the data were analysed using the Shapiro–Wilk W-test and Levene's test, respectively. Data were analyzed using ANOVA (parametric data) or the Kruskal–Wallis test (nonparametric data) when appropriate, while means within groups were compared using Tukey's HSD test or the Kruskal–Wallis test. A statistically significant difference was considered at the level of $p \leq 0.05$ (95% confidence interval).

## 3. Results and Discussion

This study aimed to evaluate the potential of three encapsulating agents applied in different ratios at different temperatures for spray-drying encapsulation of blackthorn flower polyphenols and to observe the effect of encapsulation parameters on the retention of individual and total polyphenols in obtained powders.

To achieve the aim of the study, 45 spray-dried powders were produced according to the experimental design and identification and quantification of polyphenols was conducted by UPLC-MS/MS. All obtained powders were in a free-flowing form, with powder yield ranging from 40.17–67.21% (data not published). A total of 25 individual polyphenols were identified (Figure 1) using available standards and mass spectral data: 3-*O*-caffeoylquinic acid (neochlorogenic acid), 3-*p*-coumaroilquinic acid, chlorogenic acid, feruloylquinic acid, caffeic acid, 4-*p*-coumaroilquinic acid, and ferulic acid, belonging to the class of hydroxycinnamic acids; gallic acid as representative of hydroxybenzoic acids; procyanidin B1, catechin, and epicatechin as flavanols; kaempferol-rhamnosylhexoside, quercetin-pentosylhexoside, quercetin-3-rutinoside, quercetin-3-glucoside, quercetin-pentoside, kaempferol-3-rutinoside, kaempferol-pentosylhexoside, isorhamnetin-rutinoside, kaempferol-pentoside, quercetin-rhamnoside, kaempferol-rhamnoside, quercetin-acetylhexoside, and kaempferol-acetylhexoside from the class of flavonols; and luteolin belonging to the flavones. From the concentration range for each of the identified compounds in dependence of the applied encapsulation parameters shown in Table 1, it can be observed that flavonols were the most abundant polyphenolic class in encapsulated blackthorn flower extract, mainly represented by kaempferol and quercetin glycosides. Among them, kaempferol, quercetin pentoside, and quercetin-3-rutinoside were determined to be in the highest concentration, which is in accordance with a previous study by Elez Garofulić et al. [10]. Apart from the flavonols, hydroxycinnamic acids also represented a large proportion of the total identified polyphenols, with caffeic acid as the main representative.

**Table 1.** Mass spectrometric data and concentration range of individual polyphenols isolated from blackthorn flower extract encapsulated under different spray-drying conditions.

| | Polyphenol | Cone Voltage (V) | Collision Energy (V) | Ionization Mode | Precursor Ion (*m*/*z*) | Fragment Ions (*m*/*z*) | Concentration (mg/100 g e.d.m.) | |
|---|---|---|---|---|---|---|---|---|
| | THC | | | | | | **Min** | **Max** |
| 1 | 3-*O*-caffeoylquinic acid (neochlorogenic acid) | 80 | 10 | - | 353 | 191 | nd | 167.13 ± 4.63 |
| 2 | 3-*p*-coumaroilquinic acid | 80 | 10 | - | 337 | 163 | 73.55 ± 3.03 | 276.40 ± 7.98 |
| 3 | Chlorogenic acid * | 80 | 10 | - | 353 | 191 | 11.76 ± 0.18 | 73.67 ± 2.14 |
| 4 | Feruloylquinic acid | 80 | 5 | - | 367 | 193 | 39.16 ± 1.61 | 172.06 ± 4.77 |
| 5 | Caffeic acid * | 80 | 10 | - | 179 | 135 | 140.27 ± 2.00 | 694.96 ± 9.93 |
| 6 | 4-*p*-coumaroilquinic acid | 80 | 10 | - | 337 | 173 | nd | 130.27 ± 3.61 |
| 7 | Ferulic acid * | 80 | 5, 10 | - | 193 | 178, 134 | 3.87 ± 0.16 | 14.35 ± 0.40 |
| | THB | | | | | | | |
| 8 | Gallic acid * | 100 | 10 | - | 169 | 125 | 0.77 ± 0.01 | 17.47 ± 0.50 |
| | TFLA | | | | | | | |
| 9 | Procyanidin B1 * | 120 | 5 | + | 579 | 427 | nd | 42.03 ± 1.73 |
| 10 | Catechin * | 100 | 5, 10 | + | 291 | 165, 139 | 7.05 ± 0.15 | 75.78 ± 2.19 |
| 11 | Epicatechin * | 100 | 10 | + | 291 | 139, 123 | 13.14 ± 0.54 | 52.25 ± 1.51 |
| | TFLO | | | | | | | |
| 12 | Kaempferol-rhamnosylhexoside | 120 | 15 | + | 595 | 287 | 82.84 ± 4.51 | 124.07 ± 4.50 |
| 13 | Quercetin-pentosylhexoside | 100 | 15 | + | 597 | 303 | 57.59 ± 2.75 | 115.21 ± 3.33 |
| 14 | Quercetin-3-rutinoside * | 120 | 5 | + | 611 | 303 | 194.42 ± 2.72 | 475.31 ± 22.73 |
| 15 | Quercetin-3-glucoside * | 100 | 5 | + | 465 | 303 | nd | 96.00 ± 3.31 |
| 16 | Quercetin-pentoside | 100 | 5 | + | 435 | 303 | nd | 517.91 ± 21.33 |
| 17 | Kaempferol-3-Rutinoside * | 120 | 15 | + | 595 | 287 | 5.89 ± 0.08 | 48.54 ± 2.32 |
| 18 | Kaempferol-pentosylhexoside | 120 | 15 | + | 581 | 287 | 81.96 ± 1.77 | 158.09 ± 5.73 |
| 19 | Isorhamnetin-rutinoside | 120 | 15 | + | 625 | 317 | 9.73 ± 0.47 | 21,69 ± 0,75 |
| 20 | Kaempferol-pentoside | 120 | 5 | + | 419 | 287 | 599.05 ± 12.90 | 1140.34 ± 16.29 |
| 21 | Quercetin-rhamnoside | 100 | 5 | + | 449 | 303 | 223.57 ± 10.69 | 327.22 ± 17.80 |
| 22 | Kaempferol-rhamnoside | 120 | 5 | + | 433 | 287 | 0.69 ± 0.01 | 30.77 ± 0.89 |
| 23 | Quercetin-acetylhexoside | 100 | 15 | + | 507 | 303 | 0.91 ± 0.01 | 3.09 ± 0.04 |
| 24 | Kaempferol-acetylhexoside | 120 | 5 | + | 491 | 287 | nd | 9.95 ± 0.14 |
| | TF | | | | | | | |
| 25 | Luteolin* | 140 | 35 | + | 287 | 153 | 2.25 ± 0.09 | 12.83 ± 0.37 |

* Identification confirmed using authentic standards. THC = total hydroxycinnamic acids, THB = total hydroxybenzoic acids, TFLA = total flavanols, TFLO = total flavonols, TF = total flavones, TPC = total phenolic content.

Individual concentrations of polyphenols in all experimental trials for each of the five different wall materials/mixtures used were summed to obtain total hydroxycinnamic acids (THC), total hydroxybenzoic acids (THB), total flavanols (TFLA), total flavonols (TFLO), total flavones (TFA), and total phenolic content (TPC) (Table 2) in order to provide insight into the effect of encapsulation parameters on each of the observed polyphenolic groups (Table 3).

**Table 2.** Total hydroxycinnamic acids (THC), total hydroxybenzoic acids (THB), total flavanols (TFLA), total flavonols (TFLO), total flavons (TF), and total phenolic content (TPC) in encapsulated blackthorn flower extract obtained by spray drying using different wall materials, wall material-to-extract dry matter ratios, and drying temperatures.

| WM | WM/ e.d.m. | Td (°C) | THC mg/100 g e.d.m. | THB mg/100 g e.d.m. | TFLA mg/100 g e.d.m. | TFLO mg/100 g e.d.m. | TF mg/100 g e.d.m. | TPC mg/100 g e.d.m. |
|---|---|---|---|---|---|---|---|---|
| MD | 0.5 | 120 | 1303.95 ± 36.16 | 2.46 ± 0.03 | 122.06 ± 3.38 | 2015.11 ± 55.88 | 10.66 ± 0.30 | 3454.24 ± 95.75 |
| | | 150 | 1208.33 ± 41.68 | 2.57 ± 0.03 | 132.03 ± 4.55 | 2313.99 ± 79.82 | 6.31 ± 0.22 | 3663.23 ± 126.30 |
| | | 180 | 1317.87 ± 18.83 | 4.35 ± 0.01 | 129.07 ± 1.48 | 2763.01 ± 39.47 | 11.72 ± 0.18 | 4226.02 ± 59.97 |
| | 1 | 120 | 1094.02 ± 23.56 | 1.45 ± 0.02 | 96.60 ± 2.08 | 1923.43 ± 41.42 | 9.61 ± 0.21 | 3125.11 ± 67.29 |
| | | 150 | 1436.42 ± 52.09 | 3.14 ± 0.04 | 143.00 ± 5.19 | 2380.84 ± 86.33 | 12.13 ± 0.44 | 3975.53 ± 144.09 |
| | | 180 | 1407.80 ± 40.63 | 3.35 ± 0.03 | 156.10 ± 4.51 | 2566.54 ± 74.07 | 12.97 ± 0.37 | 4146.76 ± 119.61 |
| | 2 | 120 | 1480.84 ± 21.15 | 2.37 ± 0.01 | 124.21 ± 1.77 | 1781.23 ± 25.44 | 10.67 ± 0.15 | 3399.32 ± 48.52 |
| | | 150 | 1510.25 ± 43.59 | 2.76 ± 0.03 | 147.07 ± 4.24 | 2368.76 ± 68.37 | 12.52 ± 0.36 | 4041.36 ± 116.59 |
| | | 180 | 1324.82 ± 54.57 | 2.15 ± 0.04 | 153.72 ± 6.33 | 2033.52 ± 83.76 | 10.04 ± 0.41 | 3524.25 ± 145.11 |
| MD + 25% GA | 0.5 | 120 | 1320.13 ± 63.13 | 8.05 ± 0.05 | 137.97 ± 6.53 | 2514.66 ± 120.26 | 12.01 ± 0.57 | 3992.82 ± 190.54 |
| | | 150 | 1359.44 ± 46.89 | 8.88 ± 0.03 | 141.37 ± 4.88 | 2586.96 ± 90.54 | 12.93 ± 0.45 | 4109.58 ± 142.79 |
| | | 180 | 1452.09 ± 78.98 | 9.17 ± 0.05 | 157.83 ± 8.58 | 2533.60 ± 137.81 | 12.03 ± 0.65 | 4164.72 ± 226.07 |
| | 1 | 120 | 1446.22 ± 63.26 | 8.39 ± 0.04 | 156.24 ± 6.83 | 2542.90 ± 111.22 | 12.42 ± 0.54 | 4166.17 ± 181.89 |
| | | 150 | 1480.51 ± 42.73 | 7.68 ± 0.03 | 157.13 ± 4.53 | 2500.04 ± 72.15 | 12.22 ± 0.35 | 4157.58 ± 119.79 |
| | | 180 | 1427.67 ± 20.39 | 7.10 ± 0.01 | 162.52 ± 2.32 | 2449.53 ± 34.99 | 12.12 ± 0.17 | 4058.94 ± 57.88 |
| | 2 | 120 | 1409.64 ± 67.41 | 5.12 ± 0.05 | 115.24 ± 5.51 | 2178.08 ± 104.16 | 10.61 ± 0.51 | 3718.69 ± 177.64 |
| | | 150 | 1567.43 ± 43.46 | 6.17 ± 0.03 | 124.73 ± 3.46 | 2358.93 ± 65.41 | 11.95 ± 0.33 | 4069.21 ± 112.36 |
| | | 180 | 1531.21 ± 55.52 | 6.74 ± 0.04 | 138.66 ± 5.03 | 2417.74 ± 87.67 | 10.08 ± 0.37 | 4104.43 ± 148.63 |
| MD + 50% GA | 0.5 | 120 | 1281.43 ± 52.78 | 7.91 ± 0.04 | 133.66 ± 5.51 | 2384.97 ± 98.58 | 11.55 ± 0.48 | 3819.52 ± 157.39 |
| | | 150 | 1287.68 ± 27.73 | 10.43 ± 0.02 | 106.89 ± 2.30 | 2079.91 ± 44.79 | 9.72 ± 0.21 | 3494.63 ± 75.05 |
| | | 180 | 1254.79 ± 43.28 | 9.72 ± 0.03 | 130.55 ± 4.50 | 2149.42 ± 74.14 | 10.44 ±0.36 | 3554.92 ± 122.31 |
| | 1 | 120 | 1274.67 ± 55.75 | 7.22 ± 0.04 | 114.32 ± 5.00 | 2012.96 ± 88.04 | 6.18 ± 0.27 | 3415.35 ± 149.10 |
| | | 150 | 1151.86 ± 62.65 | 7.39 ± 0.05 | 100.63 ± 5.47 | 1811.72 ± 98.54 | 8.40 ± 0.46 | 3080.00 ± 167.17 |
| | | 180 | 1033.43 ± 29.83 | 17.47 ± 0.03 | 72.98 ± 2.11 | 2393.89 ± 69.09 | 9.29 ± 0.27 | 3527.06 ± 101.33 |
| | 2 | 120 | 1217.48 ± 58.22 | 4.88 ± 0.05 | 117.27 ± 5.61 | 1358.01 ± 64.94 | 7.98 ± 0.38 | 2705.62 ± 129.20 |
| | | 150 | 1188.13 ± 43.08 | 17.09 ± 0.04 | 86.78 ± 3.15 | 2485.07 ± 90.11 | 8.76 ± 0.32 | 3785.83 ± 136.70 |
| | | 180 | 1066.19 ± 14.93 | 15.89 ± 0.01 | 80.72 ± 1.13 | 2102.25 ± 29.44 | 7.33 ±0.10 | 3272.38 ± 45.61 |

**Table 2.** *Cont.*

| WM | WM/ e.d.m. | Td (°C) | THC mg/100 g e.d.m. | THB mg/100 g e.d.m. | TFLA mg/100 g e.d.m. | TFLO mg/100 g e.d.m. | TF mg/100 g e.d.m. | TPC mg/100 g e.d.m. |
|---|---|---|---|---|---|---|---|---|
| MD + 25 % IN | 0.5 | 120 | 1018.8 ± 41.97 | 10.27 ± 0.04 | 72.87 ± 3.00 | 1803.80 ± 74.30 | 5.73 ± 0.24 | 2911.47 ± 119.55 |
| | | 150 | 995.25 ± 47.60 | 9.94 ± 0.05 | 59.66 ± 2.85 | 1930.87 ± 92.34 | 6.94 ± 0.33 | 3002.66 ± 143.17 |
| | | 180 | 1023.06 ± 21.38 | 10.37 ± 0.02 | 64.61 ± 1.35 | 2053.29 ± 42.91 | 6.26 ± 0.13 | 3157.59 ± 65.79 |
| | 1 | 120 | 833.09 ± 45.31 | 6.87 ± 0.05 | 53.51± 2.91 | 1202.66 ± 65.42 | 4.56 ± 0.25 | 2100.69 ± 113.94 |
| | | 150 | 493.32 ± 10.62 | 0.97 ± 0.02 | 57.15 ± 1.23 | 1124.42 ± 24.22 | 3.05 ± 0.07 | 1678.90 ± 36.16 |
| | | 180 | 491.22 ± 10.27 | 0.93 ± 0.02 | 56.12 ± 1.17 | 1119.56 ± 23.46 | 3.12 ± 0.07 | 1670.95 ± 34.99 |
| | 2 | 120 | 498.52 ± 17.20 | 1.25 ± 0.03 | 57.71 ± 1.99 | 987.10 ± 34.05 | 3.06 ± 0.11 | 1547.64 ± 53.38 |
| | | 150 | 562.51 ± 20.40 | 1.58 ± 0.04 | 64.48 ± 2.34 | 1101.20± 39.93 | 3.24 ± 0.12 | 1733.01 ± 62.83 |
| | | 180 | 604.73 ± 8.47 | 1.80 ± 0.01 | 71.70 ± 1.00 | 1182.86 ± 16.5 | 3.83 ± 0.05 | 1864.92 ± 26.03 |
| MD + 50% IN | 0.5 | 120 | 327.16 ± 13.48 | 1.48 ± 0.04 | 41.10 ± 1.69 | 760.78 ± 31.34 | 2.25 ± 0.09 | 1132.77 ± 46.64 |
| | | 150 | 424.00 ± 6.06 | 0.77 ± 0.01 | 48.60 ± 0.69 | 972.13 ± 13.89 | 2.59 ± 0.04 | 1448.09 ± 20.69 |
| | | 180 | 841.06 ± 23.32 | 9.77 ± 0.03 | 51.53 ± 1.43 | 1450.89 ± 40.23 | 4.61 ±0.13 | 2357.86 ± 65.14 |
| | 1 | 120 | 763.91 ± 16.45 | 6.77 ± 0.02 | 46.84 ± 1.01 | 1276.33 ± 27.49 | 4.38 ± 0.09 | 2098.23 ± 45.06 |
| | | 150 | 970.54 ± 49.78 | 12.84 ± 0.05 | 54.98 ± 2.82 | 1634.77 ± 83.85 | 6.22 ± 0.32 | 2679.35 ± 136.82 |
| | | 180 | 948.52 ± 34.39 | 9.55 ± 0.04 | 52.74 ± 1.91 | 1553.12 ± 56.32 | 5.94 ± 0.22 | 2569.87 ± 92.88 |
| | 2 | 120 | 1059.04 ± 15.13 | 9.65 ± 0.01 | 68.92 ± 0.98 | 1789.85 ± 25.57 | 6.34 ± 0.09 | 2933.80 ± 41.78 |
| | | 150 | 997.15 ± 20.84 | 8.25 ± 0.02 | 66.82 ± 1.40 | 1549.98 ± 32.39 | 5.27 ± 0.11 | 2627.47 ± 54.76 |
| | | 180 | 1253.22 ± 34.75 | 11.41 ± 0.03 | 66.15 ± 1.83 | 1841.90 ± 51.08 | 6.91 ±0.19 | 3179.59 ± 87.88 |

The results are expressed as mean value ± standard deviation mg/100 e.d.m. WM = wall material, WM/e.d.m = wall material-to-extract dry matter ratio, Td = drying temperature. MD = maltodextrin, GA = gum arabic, IN = inulin. TPC concentrations ranged from (1132.77 ± 46.64) to (4226.02 ± 59.97) mg/100 g e.d.m. with an average amount of 3143.51 mg/100 g e.d.m.

**Table 3.** The effect of spray-drying encapsulation parameters on total hydroxycinnamic acids (THC), total hydroxybenzoic acids (THB), total flavanols (TFLA), total flavonols (TFLO), total flavones (TF), and total phenolic content (TPC) in encapsulated blackthorn flower extract.

| Encapsulation Parameters | N | BAC (mg/100 g Extract Dry Matter) | | | | | |
|---|---|---|---|---|---|---|---|
| | | THC | THB | TFLA | TFLO | TF | TPC |
| **WM** | | $p < 0.01$ + | $p < 0.01$ + | $p < 0.01$ + | $p < 0.01$ + | $p < 0.01$ + | $p < 0.01$ + |
| MD | 18 | (1342.70 ± 31.24) $^{b,c}$ | (2.73 ± 0.19) $^{a}$ | (133.76 ± 4.33) $^{b,c}$ | (2238.49 ± 74.31) $^{b}$ | (10.74 ± 0.46) $^{b,c}$ | (3728.43 ± 89.58) $^{b,c}$ |
| MD + 25% GA | 18 | (1443.82 ± 20.18) $^{c}$ | (7.48 ± 0.31) $^{b,c}$ | (143.35 ± 3.86) $^{c}$ | (2453.61 ± 32.91) $^{b}$ | (11.82 ± 0.22) $^{c}$ | (4060.07 ± 42.02) $^{c}$ |
| MD + 50% GA | 18 | (1195.07 ± 22.94) $^{b}$ | (10.89 ± 1.08) $^{c}$ | (104.87 ± 4.96) $^{b}$ | (2087.38 ± 80.43) $^{b}$ | (8.85 ± 0.38) $^{b}$ | (3407.06 ± 82.98) $^{b}$ |
| MD + 25% IN | 18 | (724.50 ± 55.08) $^{a}$ | (4.89 ± 1.00) $^{a,b}$ | (61.98 ± 1.62) $^{a}$ | (1389.88 ± 95.03) $^{a}$ | (4.42 ± 0.35) $^{a}$ | (2185.66 ± 149.31) $^{a}$ |
| MD + 50% IN | 18 | (842.73 ± 68.47) $^{a}$ | (7.83 ± 0.96) $^{b,c}$ | (55.30 ± 2.27) $^{a}$ | (1425.53 ± 83.28) $^{a}$ | (4.95 ± 0.38) $^{a}$ | (2336.34 ± 154.33) $^{a}$ |
| WM/e.d.m. | | $p = 0.51$ | $p = 0.33$ | $p = 0.94$ | $p = 0.29$ | $p = 0.86$ | $p = 0.71$ |
| 0.5 | 30 | (1094.34 ± 60.46) $^{a}$ | (7.08 ± 0.65) $^{a}$ | (101.89 ± 7.27) $^{a}$ | (2021.44 ± 104.34) $^{a}$ | (8.38 ± 0.65) $^{a}$ | (3233.12 ± 170.17) $^{a}$ |
| 1 | 30 | (1083.55 ± 60.43) $^{a}$ | (6.74 ± 0.81) $^{a}$ | (98.72 ± 8.22) $^{a}$ | (1899.72 ± 99.70) $^{a}$ | (8.18 ± 0.65) $^{a}$ | (3096.91 ± 165.61) $^{a}$ |
| 2 | 30 | (1151.41 ± 64.16) $^{a}$ | (6.47 ± 0.92) $^{a}$ | (98.95 ± 6.07) $^{a}$ | (1835.77 ± 90.65) $^{a}$ | (7.91 ± 0.56) $^{a}$ | (3100.50 ± 153.76) $^{a}$ |
| Td (°C) | | $p = 0.92$ | $p = 0.13$ | $p = 0.63$ | $p = 0.13$ | $p = 0.76$ | $p = 0.28$ |
| 120 | 30 | (1088.59 ± 62.37) $^{a}$ | (5.61 ± 0.56) $^{a}$ | (97.13 ± 6.68) $^{a}$ | (1769.33 ± 98.92) $^{a}$ | (7.87 ± 0.62) $^{a}$ | (2968.54 ± 162.66) $^{a}$ |
| 150 | 30 | (1108.86 ± 66.66) $^{a}$ | (6.70 ± 0.86) $^{a}$ | (99.42 ± 7.03) $^{a}$ | (1946.64 ± 99.96) $^{a}$ | (8.15 ± 0.66) $^{a}$ | (3169.76 ± 171.04) $^{a}$ |
| 180 | 30 | (1131.84 ± 56.13) $^{a}$ | (7.99 ± 0.88) $^{a}$ | (103.00 ± 7.93) $^{a}$ | (2040.95 ± 92.56) $^{a}$ | (8.45 ± 0.58) $^{a}$ | (3292.23 ± 151.28) $^{a}$ |
| "Grand mean" | 90 | 1109.76 ± 35.37 | 6.76 ± 0.46 | 99.85 ± 4.14 | 1918.98 ± 56.75 | 8.15 ± 0.36 | 3143.51 ± 93.47 |

The results are expressed as mean value ± standard error of the mean mg/100 e.d.m. Values with a different lower-case letter in superscript within the same column are significantly different from each other according to the Tukey HSD/Kruskal–Wallis test at $p < 0.05$. + = the factor is significant in the multifactor analysis.

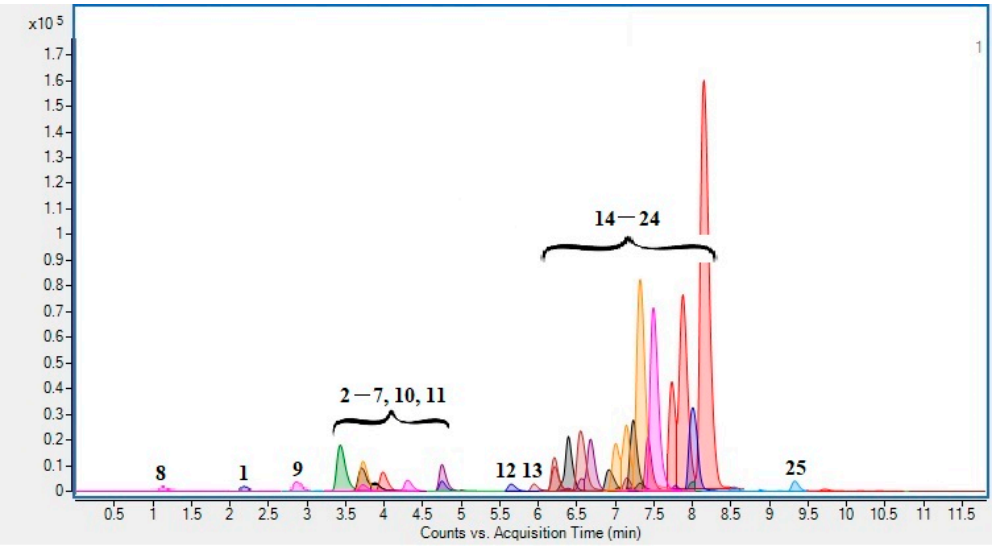


**Figure 1.** UPLC-MS/MS chromatogram in MRM acquisition mode of blackthorn flower extract encapsulated by spray-drying using MD + 25%GA as wall material in WM/e.d.m. ratio 0.5 at 120 °C: (1) 3-O-caffeoylquinic acid (neochlorogenic acid), (2) 3-*p*-coumaroilquinic acid, (3) chlorogenic acid, (4) feruloylquinic acid, (5) caffeic acid, (6) 4-*p*-coumaroilquinic acid, (7) ferulic acid, (8) gallic acid, (9) procyanidin B1, (10) catechin, (11) epicatechin, (12) kaempferol-rhamnosylhexoside, (13) quercetin-pentosylhexoside, (14) quercetin-3-rutinoside, (15) quercetin-3-glucoside, (16) quercetin-pentoside, (17) kaempferol-3-rutinoside, (18) kaempferol-pentosylhexoside, (19) isorhamnetin-rutinoside, (20) kaempferol-pentoside, (21) quercetin-rhamnoside, (22) kaempferol-rhamnoside, (23) quercetin-acetylhexoside, (24) kaempferol-acetylhexoside, (25) luteolin.

Lovrić et al. [8] reported TPC of blackthorn flower extract in a range from 45.2 to 63.7 mg/g, while the average amount was 54.1 mg/g in all extracts. The authors also reported flavonols as the most abundant polyphenolic class, with a concentration of 20.6 mg/g. Marchelak et al. [9] reported the TPC of blackthorn flower extract from Poland to reach 584.07 mg/g dry weight, total flavonols as the predominant polyphenol group

in a concentration of 490.63 mg/g dry weight, and a total phenolic acid concentration of 66.77 mg/g dry weight. These studies found a higher content of polyphenols in blackthorn flower extract than those determined in the encapsulated extracts in our study. However, significant differences have to be taken into account as these reports are referring to a TPC content determined spectrophotometrically, which is in general higher than those determined by chromatographic techniques due to a lower selectivity of the Folin–Ciocalteu method toward polyphenols and the presence of interfering compounds [37–39]. A study by Elez Garofulić et al. [10] applied the same methodology as the present report and found the TPC in blackthorn flower extract isolated by ultrasound-assisted extraction to be 2589.81 mg/100 g, which can be related to our work.

As shown in the results of the statistical analysis in Table 3, the influence of the type of wall material used for encapsulation on all observed polyphenolic groups was significant ($p < 0.01$), while wall material-to-extract dry material ratio and drying temperature had no statistically significant effect ($p > 0.05$).

Although MD is a very good encapsulation wall material for polyphenol retention in blackthorn flower extract, the best results were achieved with the addition of GA to MD. The highest concentrations of THC, TFLA, TF, and TPC were achieved with the addition of 25% of GA in MD. Similar observations were made by Tuan et al. [27], who encapsulated total polyphenols from guava leaf extract using MD and mixtures of GA and MD; better retention was achieved with the wall-material blend (9237.3 mg GAE/100 g dried basis) than when MD was used alone (8250.6 mg GAE/100 g dried basis). Busch et al. [39] encapsulated propolis polyphenols by spray drying with MD and mixtures of GA and MD, showing that the addition of GA to MD improved the encapsulation of total polyphenols. The positive effect of adding GA to MD (MD/13%GA) was as also confirmed by Navarro-Flores et al. [24]. The microencapsulation efficiency of polyphenols from chipilin leaves by spray drying was around 20% higher when an MD/GA mixture was used (85.95%) in comparison to the retention in powders obtained only with MD (65.40%). The addition of GA compensated for MD's deficiencies; namely, it improved its poor emulsification and film-forming properties when used alone [40,41], which resulted in better polyphenol retention.

Only THB were preserved the best with 50% GA, while the effect of GA on retention of TFLO was not evident. THB in blackthorn flower are represented only by gallic acid. While gallic acid is more stable than other polyphenols under strong light conditions and even high temperatures, it is unstable under strong oxidation conditions [42]. Adding more GA to the MD/GA wall material mixture increases the oxidation resistance of gallic acid during encapsulation by spray drying. This can be explained by the fact that the addition of more protein fractures of wall material in the mixture provided a protective physical barrier because protein tends to accumulate on the surface of the carbohydrate-protein powder [43], which is related to the fact that GA is a heteropolysaccharide with about 2% protein in its structure. Gimbun et al. [44] verified that gallic acid encapsulated with a mixture of whey protein isolate and MD (WPI-MD) yielded the best retention (88.93%) compared to that encapsulated by MD or WPI alone.

Tomsone et al. [45] confirmed that a high proportion of GA in an MD/GA (3:2) wall material mixture didn't improve the retention of polyphenols from horseradish leaves.

Our findings were also confirmed by Bednarska and Janiszewska-Turak [46], who encapsulated polyphenols from chokeberry juice by spray drying using MD 15.6 DE and an MD/GA mixture. With the addition of GA in an MD/GA 3:1 ratio, the concentration of polyphenols significantly increased, from 2332 to 3227 mg/100 g.d.m., while in mixtures of MD/GA with a 1:1 ratio of wall materials, polyphenol concentration decreased to 3022 mg/100 g.d.m. at a temperature of 160 °C.

Unlike the addition of GA, mixtures of MD with IN did not show a positive effect on the retention of polyphenols. The lowest concentrations of all polyphenol groups were achieved in powders with IN, being almost two-fold lower than in MD + 25%GA mixtures. Do Carmo et al. [47] confirmed that retention of betalains in spray-dried beetroot extract was higher in powders with MD (91.6%) than in one produced with MD/IN (88.45%).

Dobrinčić et al. [48] also confirmed the highest polyphenol retention (56.50%) in powders of olive leaf extract was produced with a mixture of maltodextrin and gum arabic, while very low polyphenol retention (28.24%) was achieved with inulin.

The WM/e.d.m. ratio did not affect the retention of polyphenols in encapsulated blackthorn flower extract, indicating that the lowest applied amount of wall material (WM/e.d.m. ratio 0.5) was sufficient to effectively preserve all polyphenolic groups. Although it is expected that polyphenol retention would increase with a higher ratio of wall material in the encapsulated extract, following the main role of the wall material as protective of the polyphenols, our results showed a different trend, namely no significant change in the concentration of all observed polyphenolic classes. Therefore, it can be concluded that the amount of wall material chosen as the lowest in the experiment was sufficient for fully covering the polyphenols.

Dobrinčić et al. [48] also confirmed that the lowest polyphenols:wall material ratio (5:1) was sufficient for fully covering the polyphenols from olive leaf extract.

Similar to wall material amount, spray-drying temperature also did not show significant influence on the retention of all observed polyphenolic groups, indicating the lowest applied temperature of 120 °C is optimal for blackthorn flower extract encapsulation. The lack of a temperature effect also confirms the conclusion that even the lowest addition of the wall material selected in this study was effective in protecting the polyphenols, as consequently the increase in drying temperature did not lead to polyphenolic content decrease.

Figure 2 shows the comparison of TPC retention in blackthorn flower extract encapsulated under selected optimal conditions that enabled preservation of the highest content of most of the observed polyphenolic groups in relation to the non-encapsulated primary extract. The selected encapsulation parameters ensured the high retention of total phenolics, namely 87.87% of the content determined in the liquid extract prior to the spray drying. Similar to our realized retention, Gimbun et al. [44] reported the retention of *Phyllantus niruri* polyphenols under an optimized spray-drying encapsulation method to be 87.2%. Yeop et al. [49] and Ribeiro et al. [50] reported a polyphenol retention of about 92% in encapsulated *Labisia pumila* and elderberry flower and stem extract, respectively, confirming the suitability of the optimized spray-drying process as an encapsulation technique for the preservation of plant polyphenols. The results reported in our study, as well as in other mentioned reports, suggest that spray-drying encapsulation can provide high polyphenol retention rates, comparable to or even higher than alternative techniques such as freeze drying [51,52].

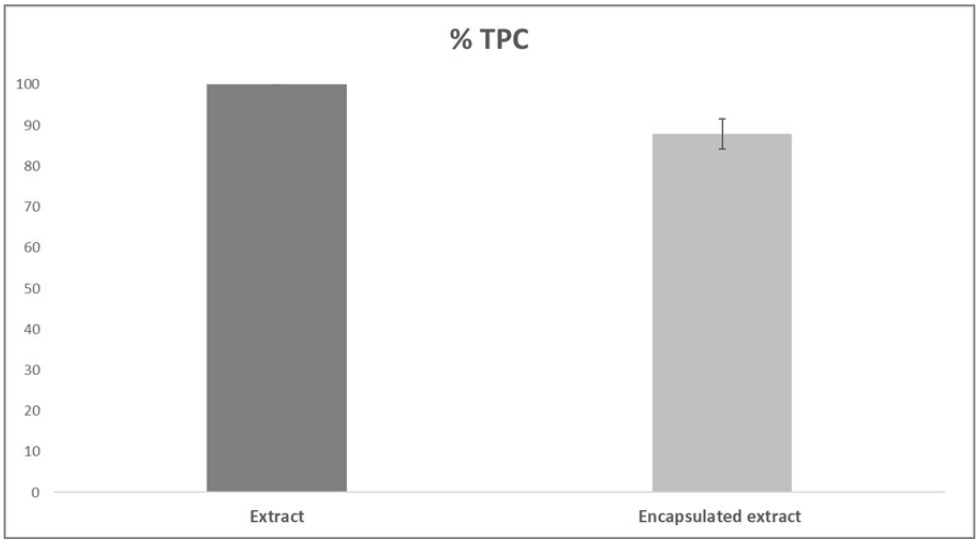


**Figure 2.** Comparison of the retention (%) of total polyphenols (TPC) in blackthorn flower extract encapsulated under optimized conditions (MD + 25%GA, WM/e.d.m. ratio 0.5, 120 °C) in relation to the total phenolic content of non-encapsulated extract.

## 4. Conclusions

The results of this study emphasize the importance of careful evaluation of spray-drying encapsulation parameters in relation to the structural differences and characteristics of different polyphenolic classes. The type of wall material applied as encapsulating agent proved to be a crucial factor determining the retention of polyphenols. Most of the observed polyphenolic groups were retained the best with 25% of gum arabic added to maltodextrin in a ratio of 0.5-to-extract dry matter and encapsulation carried out at 120 °C, with the exception of gallic acid, which favored the higher proportion of gum arabic in wall material mixture. While gum arabic addition increased polyphenolic retention, inulin had the opposite effect, thus proving not to be suitable for blackthorn flower polyphenol encapsulation. The obtained encapsulated extract retained more than 87% of polyphenols, thus representing a valuable product for future studies on its bioactivity and potential application in value-added food products. Further studies are necessary to perform characterization of the powder in terms of physicochemical properties and particle structural characteristics, as well as on powder bioactivity and bioavailability in order to create a final product for future applications.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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