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The Addition of Tomato and Spinach Powder to Semolina Pasta: A Study of the Impact of the Production Process and Cooking on Phenolic Compounds

Silvia Marzocchi [1], Federica Pasini [1,2,*], Renzo Santi [3] and Maria Fiorenza Caboni [1,2]

[1] Department of Agricultural and Food Sciences, University of Bologna, Piazza Goidanich 60, 47521 Cesena, FC, Italy; silvia.marzocchi4@unibo.it (S.M.); maria.caboni@unibo.it (M.F.C.)
[2] Interdepartmental Centre of Industrial Agri-Food Research (CIRI Agroalimentare), University of Bologna, Via Quinto Bucci 336, 47521 Cesena, FC, Italy
[3] Colussi S.p.A, Via dell'Aereoporto 7, 06081 Petrignano d'Assisi, PG, Italy; renzo.santi@colussigroup.it
* Correspondence: federica.pasini5@unibo.it; Tel.: +39-0547338117

Abstract: Pasta is a staple food with daily recommended consumption; thus, it can be an excellent vehicle for delivering bioactive compounds like phenols. However, the high-temperature drying process in pasta production, combined with cooking in boiling water, can significantly reduce the concentration of phenolic compounds. This study aimed to enhance the phenolic content of traditional semolina pasta by incorporating tomato and spinach powder into the recipe. High-performance liquid chromatography–electrospray ionization triple quadrupole mass spectrometry (HPLC-ESI-QqQ-MS) was employed to analyse the free and bound phenolic content in the raw materials, as well as in both dried uncooked and cooked pasta. The addition of tomato and spinach powders, known for their high content in bioactive compounds, increased the overall phenolic content of the final enriched pasta by three and two times, respectively, compared to the semolina and whole-wheat semolina pasta. These findings suggest that pasta enriched with tomato and spinach could serve as a functional food with a greater nutritional profile and health benefits through the enhanced delivery of phenolic compounds.

Keywords: antioxidant compounds; pasta fortification; LC-MS analysis; food processing

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1. Introduction

Pasta represents a milestone of the Mediterranean diet, occupying the base of the food pyramid, with recommended daily consumption [1]. Known for its rich carbohydrate content (31 g/100 g of cooked pasta) and energy value (154 kcal/100 g of cooked pasta), pasta, when cooked "al dente", boasts a low glycaemic index, typically ranging between 32 and 40, depending on the variety [2]. Beyond its nutritional benefits, pasta offers undeniable conveniences: it is quick to prepare, has a long shelf life, remains budget friendly, and has widespread global appeal. Therefore, pasta could be an ideal carrier of bioactive compounds, such as phenols. Conventional dry pasta production relies on two main ingredients: refined wheat semolina and water. However, most phenolic compounds, known for their antioxidant properties, are concentrated in the outer layers of the grain kernel [3,4], which are removed or reduced during the debranning and milling processes to produce refined semolina. Furthermore, the high-temperature drying step during pasta production, coupled with cooking in boiling water, can decrease the final phenolic compounds' concentration.

Many previous studies highlight the health-promoting effects of phenolic compounds, drawing significant attention in various scientific domains due to their antioxidant properties and potential protection against degenerative diseases like heart disease and cancer [5]. Phenolics include a wide range of compounds, characterized by one or more aromatic rings with one or more hydroxyl groups, and are typically classified into phenolic acids, flavonoids, stilbenes, coumarins, and tannins [6]. Phenolic acids and flavonoids, in particular, constitute the predominant forms of phenolic compounds found in cereal grains; they exist in various soluble forms, including free compounds, conjugates esterified to sugars and to other low molecular mass components, as well as insoluble bound forms [7].

Phenolic compounds also show other nutritional benefits due to their interaction with some components of pasta, such as starch and proteins. Studies report that polyphenols can modulate starch digestibility through the direct or indirect inhibition of amylolytic enzymes, representing a valid strategy for managing metabolic disorders such as obesity and type II diabetes [8]. As for protein, phenols can slow their digestion, leading to a prolonged release of amino acids, which favour metabolic conditions and promote satiety. On the other hand, excessive interactions could reduce bioavailability of important amino acids [9].

In order to enhance the functionality of semolina pasta, one approach is to use whole-wheat semolina. Whole-wheat products are widely recognized for their higher content of vitamins, minerals, antioxidants, and fibre compared to refined alternatives. Regular consumption of whole-wheat products has been linked to a reduced risk of cardiovascular disease, cancer, diabetes, and improved weight management by lowering the glycaemic response [10].

A recent and promising alternative to enrich conventional pasta is to incorporate vegetable matrices, such as tomato and spinach, into the pasta recipe.

Tomato (*Solanum lycopersicum* L.) contains several bioactive compounds such as carotenoids with various health benefits, including the mitigation of oxidative stress-related disease [11], and has a potential role in cancer and cardiovascular disease prevention [12]. Lycopene, responsible for the characteristic red colour of tomatoes and present in concentrations ranging from 850 to 12,700 µg/100 g fresh weight [13], is particularly effective in neutralizing the destructive effect of singlet oxygen [14]. Tomato is also a source of β-carotene (320–1500 µg/100 g fresh weight), a provitamin A compound, which addresses vitamin A deficiency, a leading cause of premature mortality in developing nations [13]. According to Martinez-Valverde and collaborators, tomatoes are also rich in key phenolic compounds such as quercetin, naringenin, rutin, and chlorogenic acids [15]. A study on tomato processing revealed that while some compounds like rutin and chlorogenic acids exhibit notable stability in tomato paste, others like naringenin chalcone show significant degradation [16]. On the contrary, Gahler et al. found that the total phenolic content increased during the production of both tomato juice and tomato sauce, highlighting the different impact of processing methods and environments on antioxidant components [17]. Dehydration stands as the most common processing technique for tomatoes, and a study conducted by Koh and co-authors highlighted that the hot break step results in substantial losses of flavonoids such as quercetin (54%) and kaempferol (61%), as well as reductions in ascorbic acid (63%) and β-carotene (30%) [18].

Spinach (*Spinacia oleracea* L.) is renowned for its powerful antioxidants. With respect to carotenoids, spinach is rich in lutein and zeaxanthin (5930–7900 µg/100 g fresh weight), which offer protective benefits against coronary heart disease and stroke [19]. Moreover, spinach is particularly rich in flavonoids, primarily patuletin and spinacetin derivatives, which contribute to its nutritional profile [20,21]. Factors such as genetics, maturation, the growing season, and processing methods influence the content of spinach flavonoids,

which typically ranges from 1000 to 1200 mg/kg in leaves [21–23]. In a comprehensive study by Mehmood and Zeb [24], the impact of various cooking methods on the flavonoid content in spinach leaves was thoroughly investigated. Their findings reveal significant reductions in flavonoid levels across different techniques, boiling, microwave heating, and sonication, which led to a considerable 50% decrease, while frying resulted in a 25% reduction. Interestingly, thawing showed a comparatively lower impact, with a 15% decrease in flavonoid content.

This study aimed to enrich the phenolic content of traditional semolina pasta, by incorporating tomato and spinach powder in the traditional recipe. A comprehensive analysis of free and bound phenolic compounds by HPLC coupled with mass spectrometry was performed. To the best of our knowledge, this research represents the first in-depth investigation into the effects of incorporating tomato and spinach to dry semolina pasta on its total phenolic content. This study specifically shows how these widely consumed vegetables, both rich in phenolic compounds, contribute to the phenolic profile of pasta, taking into account the effect of the pasta-making process, from raw materials to the final cooked product.

2. Materials and Methods

2.1. Samples

The raw materials used include Italian durum wheat semolina (S), Italian durum whole-wheat semolina (WWS), tomato powder (TP), and spinach powder (SP).

Four different pasta samples were formulated: one with 100% semolina (P-S), one with 100% whole-wheat semolina (P-WWS), one with 96% semolina and 4% tomato powder (P-ST), and one with 97% semolina and 3% spinach powder (P-SS). The P-S and P-WWS samples were produced in "penne rigate" format, while P-ST and P-SS were produced in "fusilli" format. The percentages of the vegetable powders were chosen after previous evaluation and sensory acceptance analyses.

The semolina and whole-wheat semolina used in these formulations complied with all legal limits and requirements for pasta production (DPR n. 187/01). Specifically, the semolina reported a moisture content below 14.5%, a protein content exceeding 13.5% (dry weight, dw), and an ash content below 0.88% (dw), and whole-wheat semolina had a moisture content below 14.5%, a protein content exceeding 13.5% (dw), and an ash content ranging between 1.40 and 1.80% (dw). For pasta enriched with tomato and spinach powders, the used semolina registered a moisture content below 14.5%, a protein content higher than 11.5% (dw), and an ash content below 0.88% (dw).

All pasta samples underwent high-temperature (HT) drying processes using an automatic drying system with humidity control (Fava S.p.A, Cento, FE, Italy); P-S was dried at 79 °C for 200 min, P-WWS at 77 °C for 200 min, and both P-ST and P-SS at 78 °C for 200 min. The small temperature variation was due to the different pasta formats and also the different production lines used for these commercial pasta products. The raw materials and pasta samples were formulated and supplied by the Italian food industry Colussi S.p.A (Perugia, PG, Italy).

2.2. Cooking of Pasta

To isolate the free and bound phenolic fractions from cooked pasta, 10 g of dried pasta was cooked in 400 mL of water for 13 min. The optimum cooking time for each sample was determined using the AACC method 66-50.26 [25]. Cooked pasta samples were freeze-dried, then milled using a laboratory mill (IKA A10-Ikawerke GmbH & Co. KG, Staufen, Germany).

2.3. Extraction of Free and Bound Phenolic Compounds

The free and bound phenolic fractions from the semolina, vegetable matrices, and pasta samples were isolated using the protocol of Verardo et al. [26], with slight modifications. Briefly, 3 g of the sample was milled with a laboratory mill (IKA A10-Ikawerke GmbH & Co. KG, Staufen, Germany) and extracted twice in an ultrasonic bath at 40 °C with 40 mL of ethanol/water (4:1, *v*/*v*) for 10 min. The supernatants were collected, evaporated at 40 °C in a rotary evaporator, and reconstituted with 2 mL of methanol/water (1:1, *v*/*v*). The extracts were stored at −18 °C until use. Residues of the free phenolic extraction were digested with 300 mL of 2 M of NaOH at room temperature for 18 h by shaking, as reported by Verardo et al. [26], with slight modifications. The mixture was acidified (pH 2–3) with hydrochloric acid in a cooling ice bath, and the final solution was extracted three times with 100 mL of ethyl acetate. The organic fractions were pooled and evaporated to dryness at 40 °C in a rotary evaporator. The phenolic compounds were finally reconstituted in 2 mL of methanol/water (1:1, *v*/*v*) and stored at −18 °C until use. Both extractions, free and bound phenols, were performed in two replicates (n = 2).

2.4. Determination of Free Phenolic Compounds with HPLC-ESI-QqQ-MS

The separation of free phenolic compounds was carried out in accordance with Borgonovi et al. [27], with some modifications. The liquid chromatography apparatus used was the 1290 Infinity Series, equipped with a binary pump delivery system (mod. G4220B), a thermostatted column compartment (mod. G1316C), and an autosampler (mod. G4226A). The HPLC system was coupled with a 6420 triple quadrupole mass spectrometer (mod. G6420A). Both the HPLC system and mass spectrometer were from Agilent Technologies (Santa Clara, CA, USA). A Poroshell 120 SB-C18 (3.0 × 100 mm, 2.7 µm) column from Agilent Technologies (Santa Clara, CA, USA) was used for compound separation; the column temperature was maintained at 35 °C during analyses. A gradient elution was programmed using, as mobile phase A, acidified water (1% acetic acid) and, as mobile phase B, acetonitrile. The following multistep linear gradient was applied: 0 min, 5% B; 12.5 min, 30% B; 17.5 min, 60% B; and 22 min, 5% B. The initial conditions were maintained for 5 min. The flow rate was set to 0.6 mL/min throughout the gradient. The injection volume in the HPLC system was 2.5 µL.

After an optimization procedure, the following MS conditions were adopted throughout the analyses: type of analysis: multiple reaction monitoring (MRM); type of source: atmospheric pressure ionization–electrospray source (API-ES); polarity: negative; drying gas (nitrogen) temperature: 350 °C; gas flow: 13 L/min; nebulizer pressure: 50 psi; capillary voltage: +3500 V; cell accelerator voltage: 3 V; collision energy: 20 eV; and fragmentor: 85. Other parameters such as the parent ion, fragment ions, and quantification transition are specified in Table 1.

Table 1. Negative ion fragmentation data for the phenolic compounds determined in different samples of raw materials and uncooked and cooked pasta.

Compounds	$[M-H]^-$	Fragment Ions (*m*/*z*)	Quantification Transition
Phenolic acids			
Caffeic acid-*O*-hexoside 1	341	179-135	341→179
Caffeic acid-*O*-hexoside 2	341	179-135	341→179
Caffeic acid-*O*-hexoside 3	341	179	341→179
Neochlorogenic acid	353	191-179-135	353→191
Coumaric acid-*O*-hexoside	325	163-119	325→163
Cryptochlorogenic acid	353	191-173-135	353→191

Table 1. *Cont.*

Compounds	$[M-H]^-$	Fragment Ions (*m*/*z*)	Quantification Transition
Vanillic acid	167	108	167→108
Caffeic acid	179	135-107	179→135
Syringic acid	197	123	197→123
p-Hydroxybenzoic acid	137	93	137→93
4-Feruloylquinic acid	367	173	367→173
Vanillin	153	93	153→93
p-Coumaric acid	163	119	163→119
Ferulic acid	193	178-149-134	193→178
Ferulic acid isomer 1	193	178-149-134	193→178
Sinapic acid	223	164	223→164
Diferulic acid	385	341	385→341
Dicaffeoylquinic acid	515	353-335-191-173	515→353
Tricaffeoylquinic acid 1	677	515-353-191	677→515
Tricaffeoylquinic acid 2	677	515-353-173	677→515
Diferulic acid isomer 1	385	341	385→341
Diferulic acid isomer 2	385	341	385→341
Flavones-C-glycoside			
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 1	563	473-443	563→473
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 2	563	443	563→443
Coumarins (lactone)			
Coumarin	145	89-101	145→89
Flavones			
Naringenin-*C*-diglycoside	595	475-385-355	595→475
Naringenin-*O*-hexoside	433	271	433→271
Naringenin-C-hexoside	433	343-313	433→343
Naringenin-7-*O*-glucoside (prunin)	433	271-151	433→271
Naringenin	271	151-119	271→151
3,4,5-Trihydroxy-3,7-dimethylflavone	329	197	329→197
Flavonols			
Rutin-*O*-hexoside	771	609-300	771→609
Spinacetin-3-glucosyl-(1-6)-[apiosyl-(1-2)]-glucoside	801	655-345	801→655
Patuletin-3-glucosyl-(1-6)-[apyosyl(1-2)]-glucoside	787	655-331	787→655
Rutin-*O*-pentoside	741	609-300	741→609
Patuletin-diglucoside	655	331	655→331
Rutin	609	301-151	609→301
Patuletin-3-*O*-β-D-(2″-coumaroglucosyl)-(1-6)-[apiosyl-(1-2)]-glucoside	933	603-495-333	933→603
Patuletin-3-*O*-β-D-(2″-feruloylglucosyl)-(1-6)-[apiosyl-(1-2)]-glucoside	963	333	963→333
Spinacetin-3-*O*-β-D-glucopyranosyl-(1-6)-glucopyranoside	669	507-345	669→507
Spinacetin-3-(2″-coumaroglucosyl)-(1-6)-[apiosyl-(1-2)]-glucoside	947	347-309-177	947→347
Spinacetin-3-(2″-feruloylglucosyl)-(1-6)-glucoside	847	509-347-309	847→509
Kaempferol-3-*O*-rutinoside	593	285-255	593→285
Spinacetin-3-(2″-feruloylglucosyl)-(1-6)-[apiosyl-(1-2)]-glucoside	977	669-345	977→669
Patuletin-3-*O*-β-D-(2″-*p*-coumaroglucosyl)-(1-6)-β-D-glucoside	801	681-333-309	801→681
Patuletin-3-*O*-β-D-(2″-feruloylglucosyl)-(1-6)-glucoside	831	501-457-333	831→501
Patuletin derivative	799	505-455-333	799→505
Patuletin derivative	829	691-493-333	829→691
Spinacetin glucuronide	521	345-330	521→345
Jaceidin glucuronide	535	359	535→359
Quercetin	301	151-121	301→151
5,3′,4′-Trihydroxy-3-methoxy-6:7-methoxylenedioxyflavone-4′-glucoronide	519	343-328	519→343
5,4′-Dihydroxy-3-methoxy-6:7-methoxylenedioxyflavone-4′-glucoronide	503	327-283	503→327
5,4′-Dihydroxy-3,3′-dimethoxy-6:7-methoxylenedioxyflavone-4′-glucoronide	533	357-342	533→357

Data were processed by the MassHunter Workstation Software—Qualitative Analysis (ver. B.06.00) from Agilent. Ferulic acid, catechin, and rutin were used as standards for quantitative purposes. Each phenolic extract was analysed twice (n = 4).

2.5. Statistical Analysis

Relative standard deviations were obtained, where appropriate, for all data collected. A one-way analysis of variance (ANOVA) was evaluated using the Statistica 8 software (2006, StatSoft, Tulsa, OK, USA). p-values lower than 0.05 were considered statistically significant using Tukey's honest significant difference (HSD) test. All chemical analyses were carried out in two replicates for each extract (n = 4 for each sample), and the analytical data were used for statistical comparisons.

3. Results and Discussion

The Individual Free and Bound Phenolic Compound Contents in Raw Materials and Uncooked and Cooked Pasta Samples

The free (FP) and bound (BP) phenolic contents of the raw ingredients and pasta samples analysed in this study are comprehensively presented in Tables 2–5. These tables provide detailed data for the four types of pasta formulations: pasta made with 100% semolina, pasta made with 100% whole-wheat semolina, pasta made with 96% semolina and 4% of tomato powder, and pasta made with 97% semolina and 3% spinach powder, respectively. Figures S1–S4 in the Supplementary Materials show the trend of the percentage content of the different phenolic classes throughout the production and cooking processes of the different pasta samples.

In accordance with the existing literature, phenolic acids and flavones were the two main classes of phenolic compounds in semolina [28–30]. As reported in Table 2, bound ferulic acid was the predominant component in semolina (71 mg/kg dw), followed by its bound isomer (22.4 mg/kg dw), and represented more than 80% of the total phenolic content. Free phenols were also detected, although in lower concentrations, with p-hydroxybenzoic acid and ferulic acid being the most abundant (7.7 and 2.2 mg/kg dw, respectively). These data are supported by various studies that confirmed the prevalence of these compounds in semolina [28,31]. Other phenolic acids were identified, in a range from 0.2 to 2 mg/kg dw, and vanillin, p-coumaric, vanillic acid, and diferulic acid were detected both in the free and bound form (Table 2). Flavones were also detected in trace amounts, represented by two free apigenin derivatives, with a total content of 1.4 mg/kg dw. The total phenolic content in the semolina amounted to 113.2 mg/kg dw, consisting of 12% free phenols and 88% bound phenols.

The uncooked P-S sample presented a similar trend observed for the semolina (S). Ferulic acid and its isomer were still the main bound phenolic acids, and p-hydroxybenzoic acid the main free one, with values similar to the S sample (71.4, 18.2, and 7.8 mg/kg dw, respectively). Most of the other identified phenolic acids and flavones presented a slight decrease compared to S, and this reduction is likely due to the high temperatures applied during the extrusion and drying of the pasta, as already reported in other studies [26]. However, no significant ($p < 0.05$) reduction (5.3%) in the total phenolic content was observed compared to the raw semolina, and the free and bound total phenols presented the same contribution (12.3% and 87.7%, respectively), suggesting a small effect of the extrusion and drying steps on these compounds.

Table 2. Free and bound phenolic compounds determined in semolina (S) and uncooked and cooked pasta made with 100% semolina (P-S), expressed in mg/kg dry weight (dw).

Compound	S		Uncooked P-S		Cooked P-S	
	FP	**BP**	**FP**	**BP**	**FP**	**BP**
Phenolic acids						
Vanillic acid	0.6 ± 0.0 a	1.0 ± 0.1 B	0.8 ± 0.0 a	1.8 ± 0.4 A	n.d.	1.2 ± 0.1 AB
p-Hydroxybenzoic acid	7.7 ± 0.9 a	0.5 ± 0.0 B	7.8 ± 0.3 a	0.2 ± 0.0 C	7.5 ± 0.2 a	0.9 ± 0.0 A
4-Feruloylquinic acid	1.1 ± 0.1 b	n.d.	1.4 ± 0.1 a	n.d.	1.5 ± 0.0 a	0.8 ± 0.0
Vanillin	0.1 ± 0.0	2.0 ± 0.2	n.d.	n.d.	n.d.	n.d.
p-coumaric acid	0.2 ± 0.0 b	1.4 ± 0.2 B	n.d.	1.4 ± 0.1 B	3.9 ± 0.1 a	2.5 ± 0.1 A
Ferulic acid	2.2 ± 0.5 a	71.0 ± 2.2 A	1.3 ± 0.1 c	71.4 ± 1.7 A	1.6 ± 0.1 b	50.2 ± 1.1 B
Ferulic acid isomer 1	n.d.	22.4 ± 0.4 A	n.d.	18.2 ± 0.5 B	n.d.	n.d.
Diferulic acid	0.3 ± 0.0 b	0.8 ± 0.0 A	0.8 ± 0.0 a	0.1 ± 0.0 C	0.3 ± 0.0 b	0.3 ± 0.0 B
Diferulic acid isomer 1	n.d.	0.4 ± 0.0 B	n.d.	0.9 ± 0.0 A	n.d.	n.d.
Diferulic acid isomer 2	n.d.	0.1 ± 0.0	n.d.	n.d.	n.d.	n.d.
Flavones-C-glycoside						
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 1	0.7 ± 0.0 a	n.d.	0.5 ± 0.0 b	n.d.	0.5 ± 0.0 b	n.d.
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 2	0.7 ± 0.0 a	n.d.	0.6 ± 0.0 b	n.d.	0.1 ± 0.0 c	n.d.
Total (single fraction)	13.6 ± 1.5 a	99.6 ± 3.1 A	13.2 ± 0.5 a	94.0 ± 2.7 A	15.4 ± 0.4 a	55.9 ± 1.3 B
Total (FP + BP)	113.2 ± 4.6 a		107.2 ± 3.2 a		71.3 ± 1.7 b	

Abbreviations: FP, free phenol; BP, bound phenol; n.d.: not detected. Data are expressed as means ± standard deviation (n = 4). Different lowercase letters in the same row mean significant differences ($p < 0.05$) among free phenolic compounds; different capital letters in the same row mean significant differences ($p < 0.05$) among bound phenolic compounds.

Table 3. Free and bound phenolic compounds determined in whole-wheat semolina (WWS) and uncooked and cooked pasta made with 100% whole-wheat semolina (P-WWS), expressed in mg/kg dry weight (dw).

Compound	WWS		Uncooked P-WWS		Cooked P-WWS	
	FP	**BP**	**FP**	**BP**	**FP**	**BP**
Phenolic acids						
Vanillic acid	0.2 ± 0.0	0.6 ± 0.0 A	n.d.	0.3 ± 0.0 B	n.d.	0.2 ± 0.0 C
Syringic acid	2.2 ± 0.4 a	4.4 ± 0.5 A	0.7 ± 0.0 b	3.6 ± 0.2 B	0.4 ± 0.0 c	2.7 ± 0.2 C
p-Hydroxybenzoic acid	n.d.	3.4 ± 0.3 A	n.d.	1.2 ± 0.3 B	n.d.	0.3 ± 0.0 C
4-Feruloylquinic acid	1.2 ± 0.1 a	n.d.	1.1 ± 0.1 a	n.d.	0.9 ± 0.0 b	n.d.
Vanillin	n.d.	0.5 ± 0.0 B	n.d.	0.8 ± 0.1 A	n.d.	0.3 ± 0.0 C
p-coumaric acid	0.7 ± 0.1 a	2.2 ± 0.1 A	0.8 ± 0.1 a	0.6 ± 0.0 B	0.8 ± 0.0 a	0.7 ± 0.0 B
Ferulic acid	0.9 ± 0.1 a	74.0 ± 3.1 A	0.6 ± 0.0 b	28.1 ± 1.6 B	0.5 ± 0.0 c	14.2 ± 0.8 C
Ferulic acid isomer 1	n.d.	34.1 ± 2.0 A	n.d.	32.3 ± 1.9 A	n.d.	22.5 ± 1.4 B
Sinapic acid	n.d.	2.0 ± 0.2 B	n.d.	3.3 ± 0.4 A	n.d.	3.5 ± 0.1 A
Diferulic acid	0.6 ± 0.0 b	n.d.	0.6 ± 0.0 b	n.d.	0.8 ± 0.1 a	n.d.
Coumarins (lactone)						
Coumarin	0.3 ± 0.0 c	0.5 ± 0.0 B	0.8 ± 0.1 a	0.8 ± 0.0 A	0.5 ± 0.0 b	0.3 ± 0.0 C
Flavones-C-glycoside						
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 1	1.6 ± 0.1 a	n.d.	1.2 ± 0.1 b	n.d.	0.9 ± 0.0 c	n.d.
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 2	1.1 ± 0.0 a	n.d.	1.1 ± 0.1 a	n.d.	0.7 ± 0.0 b	n.d.
Flavones						
3,4,5-trihydroxy-3,7-dimethylflavone	9.6 ± 0.8 a	19.1 ± 1.1 A	6.4 ± 0.5 b	13.6 ± 0.9 B	7.5 ± 0.4 b	9.1 ± 0.7 C
Total (single fraction)	18.4 ± 1.6 a	140.8 ± 7.3 A	13.3 ± 1.0 b	84.6 ± 5.4 B	13.0 ± 0.5 b	53.8 ± 3.2 C
Total (FP + BP)	159.2 ± 8.9 a		97.9 ± 6.9 b		66.8 ± 3.7 c	

Abbreviations: FP, free phenol; BP, bound phenol; n.d.: not detected. Data are expressed as means ± standard deviation (n = 4). Different lowercase letters in the same row mean significant differences ($p < 0.05$) among free phenolic compounds; different capital letters in the same row mean significant differences ($p < 0.05$) among bound phenolic compounds.

Table 4. Free and bound phenolic compounds determined in the raw material semolina:tomato powder (96:4) (S + TP) and uncooked and cooked pasta made with 96% semolina and 4% tomato powder (P-ST), expressed in mg/kg dry weight (dw).

Compound	S+TP		Uncooked P-ST		Cooked P-ST	
	FP	**BP**	**FP**	**BP**	**FP**	**BP**
Phenolic acids						
Caffeic acid-*O*-hexoside 1	21.7 ± 0.2 a	6.6 ± 0.2 A	13.3 ± 0.3 b	3.3 ± 0.3 B	4.3 ± 0.6 c	n.d
Caffeic acid-*O*-hexoside 2	12.5 ± 0.6 a	9.3 ± 0.6 A	10.0 ± 1.0 b	3.5 ± 0.4 B	6.4 ± 0.7 c	2.2 ± 0.2 C
Caffeic acid-*O*-hexoside 3	1.2 ± 0.1	n.d	n.d	n.d	n.d	n.d
Neochlorogenic acid	12.9 ± 0.8 a	n.d	8.9 ± 0.8 b	n.d	6.2 ± 0.5 c	n.d
Coumaric acid-*O*-hexoside	0.7 ± 0.0 a	1.6 ± 0.1	0.8 ± 0.1 a	n.d	n.d	n.d
Cryptochlorogenic acid	12.0 ± 1.5 a	n.d	7.4 ± 0.5 b	n.d	3.7 ± 0.5 c	n.d
Vanillic acid	31.2 ± 2.8	4.8 ± 0.7 A	n.d	3.6 ± 0.9 A	n.d	n.d
Caffeic acid	4.5 ± 0.8 a	76.0 ± 1.5 A	1.5 ± 0.2 b	n.d	0.9 ± 0.0 c	n.d
p-Hydroxybenzoic acid	2.9 ± 0.8 a	4.6 ± 0.8 A	0.9 ± 0.0 b	2.7 ± 0.4 B	n.d	n.d
4-Feruloylquinic acid	n.d	18.7 ± 0.5 A	n.d	9.1 ± 0.4 B	n.d	20.4 ± 2.4 A
Vanillin	27.2 ± 2.7	4.9 ± 0.7	n.d	n.d	n.d	n.d
p-coumaric acid	1.1 ± 0.2 a	15.0 ± 0.4 A	0.5 ± 0.0 b	7.8 ± 0.8 B	n.d	4.0 ± 0.4 C
Ferulic acid	90.6 ± 9.8 a	73.8 ± 2.8 A	51.4 ± 4.1 b	46.7 ± 5.2 B	21.2 ± 2.4 c	29.0 ± 1.5 C
Ferulic acid isomer 1	n.d	62.6 ± 4.6 A	n.d	57.8 ± 3.9 B	n.d	37.3 ± 1.9 C
Diferulic acid	30.4 ± 2.6 a	27.6 ± 0.9 B	11.6 ± 0.7 b	25.4 ± 1.5 B	9.4 ± 0.9 c	36.2 ± 3.1 A
Dicaffeoylquinic acid	67.2 ± 9.7 a	n.d	35.0 ± 2.8 b	n.d	13.1 ± 0.7 c	n.d
Tricaffeoylquinic acid 1	11.1 ± 1.5 a	n.d	8.0 ± 0.9 b	n.d	0.9 ± 0.1 c	n.d
Tricaffeoylquinic acid 2	29.2 ± 2.6 a	n.d	14.9 ± 1.6 b	n.d	0.9 ± 0.2 c	n.d
Diferulic acid isomer 1	5.9 ± 0.7	n.d	n.d	n.d	n.d	n.d
Diferulic acid isomer 2	n.d	20.7 ± 1.4 B	n.d	15.2 ± 0.9 C	n.d	31.5 ± 3.0 A
Flavones						
Naringenin-*C*-diglycoside	14.0 ± 0.5	n.d	n.d	n.d	n.d	n.d
Naringenin-*O*-hexoside	17.5 ± 1.2 a	n.d	3.6 ± 0.2 b	n.d	n.d	n.d
Naringenin-*C*-hexoside	2.3 ± 0.8 a	n.d	0.5 ± 0.0 b	n.d	n.d	n.d
Naringenin-7-*O*-glucoside (prunin)	9.7 ± 0.4 a	1.1 ± 0.0	0.8 ± 0.0 b	n.d	n.d	n.d
Naringenin	31.8 ± 0.8 a	n.d	17.6 ± 1.4 b	n.d	n.d	n.d
Flavones-C-glycoside						
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 1	0.7 ± 0.0	n.d	n.d	n.d	n.d	n.d
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 2	0.7 ± 0.0	n.d	n.d	n.d	n.d	n.d

Table 4. *Cont.*

Compound	S+TP		Uncooked P-ST		Cooked P-ST	
	FP	**BP**	**FP**	**BP**	**FP**	**BP**
Flavonols						
Rutin-*O*-hexoside	13.2 ± 1.8 a	n.d	8.3 ± 0.9 b	n.d	4.2 ± 0.8 c	n.d
Rutin-*O*-pentoside	13.4 ± 0.7 a	n.d	1.1 ± 0.3 b	n.d	n.d	n.d
Rutin	56.2 ± 3.6 a	4.3 ± 0.6	18.7 ± 3.6 b	n.d	7.4 ± 0.6 c	n.d
Kaempferol-3-*O*-rutinoside	6.4 ± 0.4	0.2 ± 0.0	n.d	n.d	n.d	n.d
Quercetin	9.3 ± 0.1 a	3.8 ± 0.4 A	5.9 ± 0.8 b	2.2 ± 0.4 B	1.7 ± 0.4 c	1.3 ± 0.2 C
Total (single fraction)	537.5 ± 47.7 a	335.6 ± 16.2 A	220.7 ± 20.2 b	177.3 ± 15.1 B	80.3 ± 8.4 c	161.9 ± 13.1 B
Total FP + BP	873.1 ± 64.0 a		398.0 ± 35.3 b		242.2 ± 21.5 b	

Abbreviations: FP, free phenol; BP, bound phenol; n.d.: not detected. Data are expressed as means ± standard deviation (n = 4). Different lowercase letters in the same row mean significant differences ($p < 0.05$) among free phenolic compounds; different capital letters in the same row mean significant differences ($p < 0.05$) among bound phenolic compounds.

Table 5. Free and bound phenolic compounds determined in the raw material semolina:spinach powder (97:3) (S + SP) and uncooked and cooked pasta made with 97% semolina and 3% spinach powder (P-SS), expressed in mg/kg dry weight (dw).

Compound	S + SP		Uncooked P-SS		Cooked P-SS	
	FP	**BP**	**FP**	**BP**	**FP**	**BP**
Phenolic acids						
Vanillic acid	3.3 ± 0.5 b	7.2 ± 0.9 A	0.7 ± 0.0 a	5.6 ± 0.1 B	n.d	n.d
p-Hydroxybenzoic acid	9.2 ± 0.5	4.5 ± 0.4 A	n.d	1.4 ± 0.1 B	n.d	n.d
4-Feruloylquinic acid	1.3 ± 0.2	n.d	n.d	n.d	n.d	n.d
Vanillin	0.8 ± 0.0 c	8.6 ± 0.9 A	0.6 ± 0.0 a	1.6 ± 0.2 B	0.1 ± 0.0 b	n.d
p-coumaric acid	0.2 ± 0.0 c	79.9 ± 5.4 A	n.d	17.6 ± 1.0 B	n.d	6.6 ± 0.9 C
Ferulic acid	2.6 ± 0.1 a	173.4 ± 16.8 A	1.6 ± 0.1 b	82.6 ± 5.6 B	0.5 ± 0.1 c	86.5 ± 7.6 B
Diferulic acid	1.4 ± 0.2 c	39.5 ± 2.9 A	0.8 ± 0.1 b	31.3 ± 1.3 B	0.4 ± 0.4 a	31.7 ± 2.8 B
Flavones-C-glycoside						
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 1	0.7 ± 0.1 a	n.d	0.4 ± 0.0 b	n.d	0.8 ± 0.0 a	n.d
Apigenin-6-*C*-arabinoside-8-*C*-hexoside isomer 2	0.7 ± 0.0	n.d	n.d	n.d	n.d	n.d

Table 5. *Cont.*

Compound	S + SP		Uncooked P-SS		Cooked P-SS	
	FP	**BP**	**FP**	**BP**	**FP**	**BP**
Flavonols						
Spinacetin-3-glucosyl-(1-6)-[apiosyl-(1-2)]-glucoside	36.1 ± 5.5 a	n.d	n.d	n.d	n.d	n.d
Patuletin-3-glucosyl-(1-6)-[apyosyl(1-2)]-glucoside	85.1 ± 11.4 a	n.d	46.6 ± 2.7 b	n.d	1.8 ± 0.2 c	n.d
Patuletin-diglucoside	53.8 ± 9.9 a	n.d	18.6 ± 1.0 b	n.d	0.7 ± 0.1 c	n.d
Patuletin-3-*O*-β-D-(2″-coumaroglucosyl)-(1-6)-[apiosyl-(1-2)]-glucoside	6.2 ± 0.2	n.d	n.d	n.d	n.d	n.d
Patuletin-3-*O*-β-D-(2″-feruloylglucosyl)-(1-6)-[apiosyl-(1-2)]-glucoside	15.9 ± 1.8 a	n.d	n.d	n.d	n.d	n.d
Spinacetin-3-*O*-β-D-glucopyranosyl(1-6)-glucopyranoside	16.7 ± 1.6 a	n.d	11.3 ± 0.9 b	n.d	0.7 ± 0.0 b	n.d
Spinacetin-3-(2″-coumaroglucosyl)-(1-6)-[apiosyl-(1-2)]-glucoside	2.0 ± 0.1	n.d	n.d	n.d	n.d	n.d
Spinacetin-3-(2″-feruloylglucosyl)-(1-6)-glucoside	9.1 ± 0.9	n.d	n.d	n.d	n.d	n.d
Spinacetin-3-(2″-feruloylglucosyl)-(1-6)-[apiosyl-(1-2)]-glucoside	7.6 ± 0.9 a	n.d	n.d	n.d	n.d	n.d
Patuletin-3-*O*-β-D-(2″-p-coumaroglucosyl)-(1-6)-β-D-glucoside	15.1 ± 0.7	n.d	n.d	n.d	n.d	n.d
Patuletin-3-*O*-β-D-(2″-feruloylglucosyl)-(1-6)-glucoside	10.6 ± 0.8	n.d	n.d	n.d	n.d	n.d
Patuletin derivative	51.9 ± 5.2 a	n.d	59.0 ± 3.1 a	n.d	11.9 ± 0.8 b	n.d
Patuletin derivative	22.4 ± 2.6	n.d	n.d	n.d	n.d	n.d
Spinacetin glucoronide	61.6 ± 10.9 a	2.2 ± 0.4 A	10.9 ± 0.4 b	2.3 ± 0.1 A	0.9 ± 0.0 c	n.d
Jaceidin glucoronide	27.3 ± 2.1 a	1.0 ± 0.2	5.5 ± 0.2 b	n.d	0.6 ± 0.1 c	n.d
5,3′,4′-Trihydroxy-3-methoxy-6:7-methoxylenedioxyflavone-4′-glucoronide	25.8 ± 1.2 a	3.5 ± 0.6 A	3.5 ± 0.1 b	2.5 ± 0.2 B	0.6 ± 0.0 c	n.d
5,4′-Dihydroxy-3-methoxy-6:7-methoxylenedioxyflavone-4′-glucoronide	11.8 ± 1.0 a	0.9 ± 0.0	6.3 ± 0.8 b	n.d	0.6 ± 0.1 c	n.d
5,4′-Dihydroxy-3,3′-dimethoxy-6:7-methoxylenedioxyflavone-4′-glucoronide	17.7 ± 1.6 a	1.9 ± 0.4 A	5.3 ± 0.6 b	1.1 ± 0.3 B	0.9 ± 0.1 c	n.d
Total (single fraction)	496.9 ± 60.0 a	322.6 ± 28.9 A	171.1 ± 10.0 b	146.0 ± 8.9 B	20.5 ± 1.9 c	124.8 ± 11.3 B
Total (FP + BP)	819.6 ± 88.9 a		317.1 ± 18.9 b		145.3 ± 13.2 c	

Abbreviations: FP, free phenol; BP, bound phenol; n.d.: not detected. Data are expressed as means ± standard deviation (n = 4). Different lowercase letters in the same row mean significant differences ($p < 0.05$) among free phenolic compounds; different capital letters in the same row mean significant differences ($p < 0.05$) among bound phenolic compounds.

In contrast, a significant decrease ($p < 0.05$) was observed for the cooked P-S sample, with a reduction of 33.5%, compared to the uncooked P-S sample, and 37% compared to the raw material (S). This drop is mainly due to the significant decrease in the principal bound phenols, with a decrease to 50.2 mg/kg dw of the ferulic acid and the loss of its isomer. Furthermore, diferulic isomers were no longer detected. Conversely, the free phenolic fraction did not exhibit significant ($p < 0.05$) differences throughout the production and the cooking processes, with a concentration ranging from 13.6 to 15.4 mg/kg dw. *p*-coumaric acid was the only phenolic acid that showed an increase in the cooked P-S pasta, both in its free and bound form.

As reported in Table 3, whole-wheat semolina (WWS) and its corresponding pasta samples (P-WWS) were characterized by 10 phenolic acids, 3 flavones, and 1 lactone. Only 8 of the 10 phenolic acids were also identified in the refined semolina. Syringic and sinapic acids were present in the whole grains due to their association with the bran and germ fractions [32]. Additionally, 3,4,5-trihydroxy-3,7-dimethylflavone (flavone) and coumarin (lactone) were detected in WWS but were not found in the refined semolina.

The free phenolic fraction of WWS was largely composed of 3,4,5-trihydroxy-3,7-dimethylflavone, which amounted to 9.6 mg/kg dw. A high content of this flavone, known for its anti-inflammatory and antioxidant properties [33], was also found in the bound fraction (19.1 mg/kg dw). Syringic acid was the most abundant free phenolic acid, with a concentration of 2.2 mg/kg dw, whereas ferulic acid and its isomer 1 were the most prevalent BF, with a concentration of 74 mg/kg dw and 34 mg/kg dw, respectively. Other phenolic acids were identified in smaller quantities, from 0.5 to 4.4 mg/kg dw, and only *p*-coumaric, vanillic, and syringic acids were found both in the free and bound form. Free and bound coumarin was detected with a content of 0.3 and 0.5 mg/kg dw, respectively. The total phenolic content of WWS was slightly higher than S, reporting a similar percentage contribution of the free and bound fraction (11.6 and 88.4%, respectively).

Unlike pasta with semolina, uncooked P-WWS reported a significant ($p < 0.05$) decrease in phenol content (from 159.2 to 97.9 mg/kg dw), influenced by both a drop in the free and bound fraction. For FP, a significant low amount was observed for the two main compounds, syringic acid and 3,4,5-trihydroxy-3,7-dimethylflavone (Table 3). Their bound form also showed a decrease, along with bound ferulic acid, *p*-hydroxybenzoic acid, *p*-coumaric acid, and vanillic acid.

In cooked P-WWS, a slight decrease in some free phenolic acids was registered, but the total free phenolic content did not show significant ($p < 0.05$) differences compared to the uncooked WWS (13 and 13.3 mg/kg dw, respectively). Conversely, a similar decreasing trend throughout the pasta production and cooking process was observed for BP. Except for sinapic acid, all compounds showed a significant lower amount, reporting a total content in bound phenolic compounds equal to 53.8 mg/kg dw (Table 3).

Despite the significant decline, ferulic acid, ferulic acid isomer 1, and 3,4,5-trihydroxy-3,7-dimethylflavone were still the main bound phenols in the cooked P-WWS.

For the WWS samples, the pasta-making process resulted in a 38.5% reduction in phenolic content, and the boiling process contributed to an additional 31.8% degradation in total phenolics. The substantial loss of phenolic compounds during cooking can be attributed to the solubility of phenolics in water, where many of the free and bound phenolic acids likely leach into the cooking water, leading to their loss from the final product [26].

Combining both the free and bound phenolic fractions, the total loss of the raw WWS from the cooked P-WWS amounted to 58%, a notably higher decrease compared to the 37.5% loss observed in the refined semolina pasta. These detrimental effects of technological

processing and cooking on whole-wheat products are consistent with findings reported in the literature [34,35].

As detailed in Table 4, the free phenolic compounds (FPs) in the raw materials used for the production of the tomato powder-enriched pasta (S+TP) belong to three main classes: phenolic acids, flavones, and flavonols. These classes accounted for 67.4%, 18.6%, and 14% of the total free-phenol content, respectively. Phenolic acids were also the main class of the total bound phenols (BPs), representing 97.2% of the total phenolic content. Previous research [36,37] confirmed that the predominant phenolic compounds found in tomato powder include caffeic acid, ferulic acid, naringenin, rutin, and their derivates. The total concentration of FPs in the S+TP raw material reached 537.5 mg/kg dw, with ferulic acid being the most abundant compound (90.6 mg/kg dw), followed by dicaffeoylquinic acid (67.2 mg/kg dw), rutin (56.2 mg/kg dw), naringenin (31.8 mg/kg dw), vanillic acid (31.2 mg/kg dw), and diferulic acid (30.4 mg/kg dw). Conversely, the total BP fraction showed a lower total content equal to 335.6 mg/kg dw, with caffeic acid as the dominant compound (76.0 mg/kg dw). Ferulic acid and its isomer followed closely behind, with concentrations of 73.8 and 62.6 mg/kg dw, respectively, along with diferulic acid and its isomer (27.6 and 20.7 mg/kg dw, respectively).

The high temperatures involved in the pasta-making process resulted in significant losses of phenolic content. Specifically, 59% of the free phenols and 47% of the bound phenols were lost during processing. Despite this reduction, ferulic acid (51.4 mg/kg), dicaffeoylquinic acid (35.0 mg/kg dw), rutin (18.7 mg/kg dw), and naringenin (17.6 mg/kg dw) remained the most abundant compounds within the FP fraction. BPs exhibited a lower total content compared to FPs, with a total of 177.3 mg/kg dw; this fraction was almost exclusively composed of phenolic acids, with ferulic (46.7 mg/kg dw) and diferulic acids (25.4 mg/kg dw) being the most prevalent, together with their isomers. Caffeic acid completely disappeared, probably degraded, whereas quercetin was the only flavone detected in BPs, with a concentration of 2.2 mg/kg dw. The uncooked pasta revealed a significant reduction (54.4%) in the total (FP + BP) phenolic concentration, compared to the raw material sample.

From the uncooked P-ST to the cooked P-ST, the total FP dropped further by 63.6%, with dicaffeoylquinic acid and ferulic acid remaining the most abundant compounds (13.1 and 21.2 mg/kg dw, respectively). Notably, all the flavones, represented by naringenin and its derivatives, were completely degraded during the cooking process. On the other hand, the BP fraction did not exhibit significant differences from the uncooked samples, with a total concentration of 161.9 mg/kg dw. In particular, 4-feruloylquinic acid and diferulic acid and its isomer showed an increase in the final cooked pasta, with concentrations rising to 20.4, 36.2 and 31.5 mg/kg dw, respectively. This trend is in accordance with previous studies which reported an increase in bound phenolic acids, particularly ferulic acid, after the pasta-cooking process [26,38–40]. These same studies attributed this increase to greater extraction efficiency during the cooking process that can cause structural changes at the cellular level. Heat breaks down intracellular proteins and disrupts cell wall structures, facilitating the release of bound phenols, which would otherwise remain trapped in the matrix. Moreover, the high temperature is likely due to denatured and inactivate polyphenol oxidases, preventing them from initiating the oxidation and polymerization reactions that would lead to phenolic losses [41].

Despite the high phenolic content of the enriched raw material, only 28% of the total phenolic content (free and bound) was retained in the final cooked pasta. Nevertheless, the cooked tomato powder-enriched pasta (P-ST) showed a significant increase in phenolic compounds compared with the cooked pasta samples made with 100% semolina (P-S) and 100% whole-wheat semolina (P-WWS). The total phenolic compound content (FP + BP)

in P-ST was found to be three times higher than that of the non-enriched pasta samples, highlighting that the inclusion of tomato powder in pasta formulation makes pasta a richer source of bioactive compounds with potential antioxidant properties.

As shown in Table 5, the phenolic compounds identified in the raw material semolina:spinach powder (97:3) also belong to the three classes of phenolic acids, flavones, and flavonols. Specifically, phenolic acids, flavones, and flavonols accounted for 3.8%, 0.3, and 95.6% of the total free-phenol content, respectively. In contrast, phenolic acids represented 97% of the total bound phenols (BPs), with the remaining 3% attributed to flavonols.

For the raw material S+SP, the predominant free phenol was the flavonol patuletin-3-glucosyl-(1-6)-[apyosyl(1-2)]-glucoside, with a concentration of 85.1 mg/kg dw. In order of concentration, other flavonols followed such as spinacetin glucuronide (61.6 mg/kg dw), patuletin-diglucoside (53.8 mg/kg dw), and patuletin-derivative (51.9 mg/kg dw). These findings are in accordance with previous studies on the phenolic composition of spinach leaves by LC-MS [42,43]. In the bound phenolic fraction, ferulic acid, *p*-coumaric acid, and diferulic acid were detected as the most abundant at concentrations of 173.4, 79.9, and 39.5 mg/kg dw, respectively. These high phenolic acid contents in spinach have already been reported by other authors [44,45]. The total concentration of FPs and BPs in the S+SP raw material reached values of 496.9 and 322.6 mg/kg dw, respectively, for a total amount of 819.6 mg/kg dw.

As already seen for the tomato powder-enriched pasta, the process significantly affected ($p < 0.05$) the total phenolic content of the uncooked spinach powder-enriched pasta (P-SS). In particular, 65.6% of the free phenols and 54.7% of the bound phenols were lost during processing, bringing the total phenolic content to 171.1 mg/kg dw and 146 mg/kg dw, respectively. Most of the flavonols detected in the raw material were no longer present in the uncooked pasta sample or were present but with significantly lower contents. Nonetheless, patuletin-3-glucosyl-(1-6)-[apyosyl(1-2)]-glucoside was still the most abundant free phenol, together with spinacetin glucuronide and patuletin-diglucoside (46.6, 10.9 and 18.6 mg/kg dw, respectively). The patuletin derivative was the only compound that did not show a significant ($p < 0.05$) difference from the level found in the raw material. With respect to BPs, ferulic acid, *p*-coumaric acid, and diferulic acid were still the principal phenols but with a significant ($p < 0.05$) decrease in their concentrations compared to the raw material (82.6, 17.6, and 31.3 mg/kg dw, respectively).

The cooking process led to a further significant degradation in phenolic compounds in the P-SS sample. The concentration of free phenols dropped by 88%, reducing the total amount to just 20.5 mg/kg dw. This decrease is mainly due to the significant drop in concentration of the main flavonols, as partly already observed for the cooked pasta enriched with tomato powder. Flavonols are especially vulnerable to heat and undergo degradation when cooking pasta. Chaaban and co-workers [46] explored the thermal stability of various flavonoids, finding that flavonols, such as rutin, undergo strong degradation when exposed to temperatures above 100 °C. This degradation is attributed to the specific chemical structure of flavonols, which makes them more easily degraded at high temperatures. Furthermore, Verardo et al. [26] found the same trend in wholemeal buckwheat pasta, where all the flavonols were lost during the cooking process. All these results confirm the high thermo instability of this class of phenols, independently of the origin matrix.

On the other hand, the BP fraction exhibited a smaller decrease, with a total phenol content not significantly ($p < 0.05$) different compared to the uncooked pasta sample. The few flavonols present were all lost after cooking, while the two main phenolic acids (ferulic and diferulic acid) did not show large significant differences from the uncooked pasta. Other previous studies found this behaviour for phenolic acids in high-temperature water [47]. Cheng and co-authors demonstrated that phenolic acids remain stable in

water at temperatures up to 150 °C and are almost completely decomposed at 250 °C. The chemical structure of phenolic acids makes them more resistant to degradation at high temperatures, and consequently, their retention in cooked pasta can be preserved, contributing to the potential health benefits of the final product.

Even if the total phenolic content decreases by over 50% during cooking, an enrichment in phenolic compounds is still observed in the final cooked P-SS compared to the cooked pasta made with 100% semolina (P-S) and 100% whole-wheat semolina (P-WWS). This substantial difference indicates the key role of spinach powder in significantly improving the antioxidant potential of pasta. The Supplementary Materials (Figures S1–S4) clearly show that flavones and flavonols are the most thermolabile phenolic classes across all pasta sample, resulting in a decrease in their content in the final cooked product.

4. Conclusions

This study highlights the impact of production and cooking processes on the final phenolic content of pasta. However, the integration of ingredients rich in bioactive compounds, like tomato and spinach powders, into the pasta-making process significantly enhances the overall phenolic content of pasta. This enrichment process presents a valuable strategy for increasing the dietary intake of phenolic compounds through a common food like pasta. These findings underscore the potential of ingredient fortification as a viable strategy for producing health-promoting, nutrient-rich pasta products, making them a healthier alternative to conventional options. Future investigations will focus on optimizing the processing condition to maximize the retention of these beneficial compounds, ensuring both nutritional and sensory attributes are preserved or enhanced.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app15020634/s1, Figure S1: Concentration (%) of free, bound and total phenolic acid and flavones-*C*-glucoside determined in semolina (S), uncooked and cooked pasta made with 100% of semolina (P-S), expressed in mg/kg dry weight (dw); Figure S2: Concentration (%) of free, bound and total phenolic acid, coumarins, flavones-*C*-glucoside and flavones determined in whole wheat semolina (WWS), uncooked and cooked pasta made with 100% of whole wheat semolina (P-WWS); Figure S3: Concentration (%) of free, bound and total phenolic acid, flavones, flavones-*C*-glucoside and flavonols determined in the raw material semolina:tomato 96:4 (S+TP), uncooked and cooked pasta made with 96% of semolina and 4% of tomato powder (P-ST); Figure S4: Concentration (%) of free, bound and total phenolic acid, flavones-*C*-glucoside and flavonols determined in the raw material semolina:spinach 97:3 (S+SP), uncooked and cooked pasta made with 97% of semolina and 3% of tomato powder (P-SS).

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