



Industrial upcycling of almond skin through production of novel brioches

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ABSTRACT

The global sustainability policy emphasizes reusing of agri-food waste and by-products to enhance food bioactive properties. Thus, brioches were processed incorporating almond skin powder (ASP): control (CTR), without ASP addition; 5-ASP, with 5% (w/w) ASP; and 10-ASP, with 10% (w/w) ASP. Seven different brioches shapes were obtained for each recipe. Flavonoids were mainly detected in Tuono almond skin by Ultra-High Performance Liquid Chromatography coupled to High-Resolution Mass Spectrometry (UHPLC-HRMSMS), in particular, flavan-3-ol monomers. The ethanolic extract of Tuono almond skins contained polar lipids (oxylipins and phospholipids). Gas Chromatography–Mass Spectrometry (GC-MS) identified six major fatty acids, mainly oleic acid (48.01%). Photothermal degradation impact on bioactive compounds was evaluated using a first-order kinetic model. Antioxidant activity was studied using 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid), 2,2'-diphenyl-1-picrylhydrazyl and β -carotene bleaching test. α -amylase, α -glucosidase, and lipase inhibitory effect were also tested. The acidification of the doughs was consistent across all trials. Lactic acid bacteria and yeast levels increased. Importantly, the final products were free from undesirable microorganisms. The addition of ASP led to reduced weight loss and specific volume for all seven brioche types. Furthermore, the firmness, crumb structure, and sensory profile of the final products were noticeably influenced. Tasters clearly favoured the Treccina brioches. The production of sweet leavened baked goods was carried out in triplicate in two independent experiments. The statistical model applied to the data considered the effects of brioche shape and the addition of ASP. Kinetic data revealed that the half-life extension for both total phenol and flavonoid content was observed in the 10-ASP sample (18.00382). 10-ASP sample exhibited promising ABTS radical scavenging activity, with inhibitory concentration 50% (IC₅₀) values of 18.64 mg/mL after 9 days of photothermal degradation. Moreover, when testing 10-ASP Treccina against α -amylase and α -glucosidase, the IC₅₀ values were 198.16 and 190.23 μ g/mL, respectively, even after 9 days.

1. Introduction

The global industry of baked goods is dynamic, offering a diverse array of food choices for various times of the day, spanning from main meals to snack breaks [1]. Bakery products encompass a wide range, including breads, pizza, crispbreads, crackers, cakes, muffins, biscuits, cookies, pastries, brioches, and buns [1–5].

In Italy, rich culinary traditions have given birth to an extensive variety of baked goods, both sweet and savoury. Among the sweet leavened baked goods, brioches take centre stage. These delightful treats are produced daily and are commonly consumed for breakfast or as a snack. The key leavening agent in brioches is sourdough, a mixture of flour and water teeming with lactic acid bacteria (LAB) and active yeasts [6]. However, due to their high fat content, some sweet leavened

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products also incorporate additional baker's yeast [4].

In recent years, there has been a growing global interest in reusing agri-food waste and by-products (W&BP) to enhance the sustainability of food production chains [7]. These W&BP are increasingly recognized as valuable functional food ingredients due to their rich content of bioactive compounds [8]. Among these, nut peel stands out as a fruit-derived material that has been previously utilized in bakery products for its health-promoting effects [9–15].

Almond (*Prunus dulcis* L.), a significant crop in the food industry [16], produces a by-product of relevant interest: almond skin, which is rich in polyphenols [14,17]. Gaglio et al. [13] have highlighted that almond skin can serve as a functional ingredient compatible with wheat sourdough bread production. Additionally, Pasqualone et al. [18] successfully incorporated this functional ingredient into biscuits, which are sweet baked goods commonly consumed on a daily basis. However, despite these promising applications, almond skins have not yet been explored in the production of sweet leavened baked goods. Given that brioches are popular baked goods in many countries, they present an ideal opportunity for incorporating functional ingredients like almond skin.

Metabolic syndrome (MetS) is a complex disorder often associated with insulin resistance, high cholesterol and triglycerides levels, and abdominal obesity [19]. It is well known that the hyperglycaemic condition in MetS is linked to an increased production of reactive oxygen species (ROS), leading to oxidative stress and contributing to the disease's pathogenesis and progression [20]. Given the intricate nature of MetS, effective treatment remains a pressing research challenge. One of the most widely applied approaches for MetS prevention involves the consumption of functional foods. These foods have the potential to prevent or reduce the incidence of MetS. Experimental evidence suggests that bioactive compounds found in functional foods can play a crucial role. Specifically, these compounds, often belonging to the class of phenols, exhibit several beneficial effects: improved glucose tolerance by enhancing insulin sensitivity; reduced dyslipidemia because they contribute to better lipid profiles; antioxidant properties combating oxidative stress; and weight management because some compounds aid in weight loss or prevent weight gain [21,22]. Additionally, the inhibition of carbohydrate hydrolysing enzymes (α -amylase and α -glucosidase), and pancreatic lipase was one of the most applied preventing approaches to counteract MetS and obesity. In fact, the inhibition of carbohydrate hydrolysing enzymes delays the carbohydrate digestion with a consequent hypoglycaemic effect, whereas the inhibition of pancreatic lipase reduces the absorption of ingested fats with a consequent hypolipidemic effect [23,24].

The aim of this study is to explore the impact of incorporating almond skin by-products into various typical brioches produced at an industrial level in Sicily. To achieve this purpose, the chemical characterization of the *n*-hexane and ethanolic (EtOH) extract of the almond skin from "Tuono" cultivar was performed by gas chromatography mass spectrometry (GC-MS) and ultra-high-performance liquid chromatography coupled to mass spectrometer (UHPLC-HRMSMS) with the aim to identify compounds responsible of the bioactivity. Almond skin enriched brioches were subjected to physicochemical, microbiological, and sensory analysis. The typology of brioche mostly preferred by judges was also analysed for its total phenols (TPC) and flavonoids (TFC) content, antioxidant activity, carbohydrate hydrolysing enzymes and pancreatic lipase inhibitory activities. The impact of photothermal aging for 9 days on this brioche was assessed to validate the reuse of almond by-products in sweet leavened baked good production.

2. Materials and methods

2.1. Almond skin powder production

Wet almond skin was collected from the factory "Bongiovanni Almonds s.r.l.", located in Mazzarino (CL, Italy), just after peeling of

almonds from the cultivars "Casteltermeni" and "Tuono", treated separately. Peeling occurred by blanching (95 °C for 3 min) the unpeeled seeds. Wet peel of both cultivars was separately transferred into polyethylene bags and immediately frozen (−20 °C). To avoid complete defrosting, almond masses were transported in thermal insulated boxes containing reusable ice packs to the Department of Agricultural, Food and Forestry Sciences (SAAF) – University of Palermo – for powdering. Equal amounts of almond skin of "Casteltermeni" and "Tuono" cultivars were mixed and loaded at a biomass density of 2.5 kg/m² on stainless steel trays. Drying was performed by convection at 54 °C in the oven mod. E34 WTB-Binder (BINDER GmbH, Tuttlingen, Germany) until a constant weight was reached. Water activity (a_w) was determined with the Rotronic Hygropalm HC2-AW (Rotronic AG, Bassersdorf, Switzerland). Dried almond skin was milled at 250 μ m through the Fritsch Mill Pulverisette 14 centrifugal apparatus (Fritsch GmbH, Idar-Oberstein, Germany). The resulting almond skin powder (ASP) was aliquoted (500 g), vacuum packed and stored at room temperature in a laboratory closet.

2.2. *n*-Hexane and ethanol extraction of "Tuono" almond skin

About five hundred grams (500 g) of fresh "Tuono" cultivar almond skin were freeze-dried to give 180 g of dry material. Then, the dry materials were extracted by a conventional Soxhlet extractor (3 h) with *n*-hexane to give, after solvent evaporation, 15.2 g of oil (yield 8.4%). A part of the residue defatted in *n*-hexane (\approx 100 g) was subjected to subsequent ethanolic extraction using absolute ethanol (\geq 99.8%) and carrying out three sequential static extractions (3 times \times 100 mL) to give a 7.4 g of dry extract (yield 7.4%).

2.3. Chemical characterization of *n*-hexane extraction: Gas Chromatography–Mass Spectrometry (GC–MS) analysis

n-Hexane extract was subjected to basic *trans*-methylation using potassium hydroxide in methanol before the injection in a Hewlett-Packard gas chromatograph (GC) (Agilent, Milan, Italy) equipped with a non-polar HP-5MS capillary column (30 m \times 0.25 mm, 0.25 μ m), and associated with a Hewlett-Packard mass spectrometer (MS) (Agilent, Milan, Italy) [25]. The ionization of the sample constituents was performed in electronic impact (EI, 70 eV). The analyses were carried out with the following temperature schedule: isothermal 50 °C for 5 min, temperature increase from 50 to 250 °C at 5 °C/min, and finally isothermal 250 °C for 10 min. Helium was used as a carrier gas. Kovats' retention indices (KI) were determined by using retention times of methyl esters (FAMES) and the peaks were identified by comparison with the spectral data of a standard mixture of FAMES and by comparison of their relative retention indices with WILEY275, NIST 17, ADAMS, and FFNSC2 libraries.

2.4. Chemical characterization of ethanolic extraction: UHPLC-HRMSMS analysis

The EtOH extract of "Tuono" almond skin were dissolved in methanol at a concentration of 0.5 mg/mL (injection 8 μ L) and submitted to Ultra-High Performance Liquid Chromatography coupled to High-Resolution Mass Spectrometry (UHPLC-HRMSMS) analysis using ultra-high-performance liquid chromatography coupled to Q-Exactive hybrid quadrupole-Orbitrap mass spectrometer (UHPLC-Q-Orbitrap) (Agilent, Milan, Italy) equipped with a heated electrospray ionization probe (HESI), in negative ion mode. For chromatographic separation, a Phenomenex Luna C₁₈ (150 \times 2.1 mm; 5 μ m) column (Phenomenex, Castel Maggiore, Italy) was used as stationary phase and H₂O + 0.1% formic acid and CH₃CN + 0.1% formic acid as mobile phases A and B, respectively, at a flow rate of 0.2 mL/min were selected. The following gradient was applied: 0–30 min, from 5 to 95% (B); then, 5 min at 95% (B) and back to 5% (B) for 5 min. The auxiliary gas was set at 10

Table 1
Recipes for doughs.

Doughs	Ingredients								
	Flour (g)	ASP (g)	Sourdough (g)	Baker's yeast (g)	Butter (g)	Sugar (g)	Powdered milk (g)	Salt (g)	H2O (mL)
CTR	3000	0	800	150	90	180	200	45	1800
5-ASP	2850	150	800	150	90	180	200	45	1800
10-ASP	2700	300	800	150	90	180	200	45	1800

Abbreviations: ASP, almond skin in powder; CTR, control dough; 5-ASP, experimental dough enriched with 5 % (w/w) of ASP; 10-ASP, experimental dough enriched with 10 % (w/w) of ASP.

(arbitrary units), the sheath gas was set at 50 (arbitrary units), and the capillary temperature at 300 °C. A full range acquisition covering m/z 150–1400 was used. A fragmentation study was performed using the data-dependent scan mode, selecting precursor ions corresponding to the most intense peaks in the UHPLC-HRMSMS spectra. Xcalibur software version 2.1 was used for instrument control, data acquisition, and data analysis [26].

2.5. Bakery leavened products

The recipes used for the production of sweet leavened doughs [CTR, control; 5-ASP, containing 5 % (w/w) ASP on the weight of flour; 10-ASP, containing 10 % (w/w) ASP on the weight of flour] are reported in Table 1. The productions of the various baked goods was carried out with the facilities of the industrial bakery “Ori di Sicilia” (Mazzarino, CL, Italy) using “00” type soft wheat flour (Industria Molitoria Denti s.r.l., Vivofertile, Italy), ASP produced in this study, baker’s yeast (“Maestro lievito per panificazione”, AB Mauri Italy S.p.A, Casteggio, Italy), butter (SA Corman, Limbourg, Belgium), kitchen sugar (Italia Zuccheri Commerciali, Minerbio, Italy), powdered milk (Laiterie de Montaigu Sas Sabourin, Cedex, France), salt (Salgamma Salvatore Bonanno, Caltagirone, Italy), tap water, and a sourdough starter propagated daily for approximately 30 years at a dough yield (DY = weight of the dough/weight of semolina × 100) 195 as follows: 10 kg of previous day sourdough mixed with 20 kg of “0” type flour (Molino F.lli Chiavazza S.p.A., Casalgrasso, Italy) and 9 L of tap water, 3 h fermentation at room temperature (approximately 20–22 °C) and refrigeration for 18 h before use.

Kneading was performed with the mixer Twist 80 S (Sottoriva S.p.A., Marano Vicentino, Italy) equipped with a spiral hook and the following program was applied: reverse rotation for 2 min at speed 1; spiral rotation for 10 min at speed 1; spiral rotation for 5 min at speed 2.

CTR, 5-ASP, and 10-ASP doughs were manually shaped by the pastry maker into seven products typical of Sicilian patisserie: Treccina; Bombolone; Cuore; Undoppio; Papillon; Ciambellina; Cavalluccio. All shaped doughs (100 g weight each) were leavened into a Maturpast chamber (Colip S.r.l., San Vincenzo Galliera, Italy) for 1 h at 28 °C and 87 % relative humidity. Baking of the leavened doughs was performed in a ventilated oven (Forni CIMAV, mod. TS6, Villafranca, Italy) at 180 °C for 10 min. The production of the brioche was performed in two consecutive weeks (two independent experimental replicates) in triplicate (three technical repeats per production).

2.6. Monitoring of the acidification of sourdough and sweet doughs

Sourdough starter was analysed for pH directly at the bakery facility by the portable pH-meter Russell RL060P (Thermo Fisher Scientific, Beverly, MA, USA) just before inoculating the sweet doughs. Samples (150 g) were collected aseptically and transferred in 200 mL volume sterile cups (Anicrin, Scorzé, Italy) for determination of total titratable acidity (TTA), lactic and acetic acid concentration, and microbiological analysis as reported by Gaglio et al. [13].

2.7. Determination of quality parameters of baked products

All products were cooled at ambient temperature for 30 min after baking and analysed for several parameters. Weight loss (WL), volume, firmness, crust and crumb color, and crumb structure of the baked products were determined as reported by Gaglio et al. [13].

2.8. Sensory profile determination and consumer's preference

All baked products were subjected to a descriptive sensory analysis with 19 panellists (11 women and eight men, 20–63 years old). All judges were trained to be familiar with the sensory attributes of sweet leavened products using commercial empty croissants purchased from a local bar. The method described by Panirani et al. [27] for bread sensory evaluation was adapted to the sweet baked goods produced in this work. Thus, slices of 2-cm thickness were cut from each product a few minutes before the tasting session and put on plastic plates reporting a three-digit code each [28]. The panellists were not allowed to visualize the entire baked products and were asked to express their judgement of the descriptors for appearance, texture, odor, taste, flavour, and mouthfeel [29,30] on a 9-point scale (1 = extremely bad; 9 = extremely good). The panellists were also asked to provide their general assessment of the sweet baked goods on the basis of the scores of all attributes. Sensory evaluation was conducted in single chambers following ISO 13299 guidelines [31].

A preference test with 87 untrained university students (19–24 years old) was performed to evaluate each shape of the baked goods produced in order to select the most appreciated product for the ASP industrial production. The judges were asked to base their choice on their personal liking and to express their preference from 1 (least preferred) to 10 (most preferred).

2.9. Degradation testing and extraction procedures

Tests were performed only on the Treccina samples, brioche with a more particular shape, presenting a greater surface area than the other samples and that obtained the highest score in the preference test.

2.9.1. Photostability test

Photostability test was simulated by UV–visible ray irradiation using SUNTEST XLS + II (Atlas®, URAI, Assago, Italy) for 24 h; SUNTEST instrument was set up in according to standard European procedures [32], with the following parameters: time: 4.5 h corresponding to 216 h solar light; irradiation control: 300–800 nm; irradiation (W/m^2): 750; room temperature: 18–26 °C; black standard temperature (BST): 45 °C; humidity: 45–65 %. Samples of almond skin, and Treccina brioche (CTR, 5-ASP, and 10-ASP) were taken from the photothermal chamber at 1.5, 3, and 4.5 h corresponding, respectively, to 3, 6, and 9 days of solar light exposition. One sample each of ASP and Treccina brioche (CTR, 5-ASP, and 10-ASP) was not subjected, instead, to thermophotometric stress (day 0).

2.9.2. Extraction procedure on almond skin and Treccina brioche

To evaluate the antioxidant power, a slightly modified extraction procedure reported by Sicari et al. [33] was used. One gram of almond

Table 2

Compounds identified in EtOH extract of “Tuono” almond skin by UHPLC-HRMSMS (negative ion mode).

No.	R _t (min)	Molecular Formula	[(M + HCOOH)–H] [–]	[M – H] [–]	Δ ppm	MS/MS	Compound
1	9.44	C ₁₅ H ₁₄ O ₆		289.1718	3.8		catechin
2	9.58	C ₄₅ H ₃₈ O ₁₈		865.1997	2.6	289	EC-b-EC-b-EC
3	10.32	C ₁₅ H ₁₄ O ₆		289.1719	4.4		epicatechin
4	10.32	C ₄₅ H ₃₈ O ₁₈		865.2003	3.3	289	EC-b-EC-b-EC
5	10.32	C ₃₀ H ₂₆ O ₁₂		577.1356	2.7	559, 407, 289	EC-b-EC
6	10.49	C ₂₁ H ₂₁ O ₁₁ ⁺		449.1094	3.6	287, 151	cyanidin-glycoside
7	10.90		C ₁₅ H ₁₈ O ₈ N	340.1037	3.0	162	prunasin
8	10.93	C ₃₀ H ₂₆ O ₁₁		561.1407	2.9	289	EA-b-EC
9	10.94	C ₃₀ H ₂₆ O ₁₂		577.1357	2.8	559, 407, 289	EC-b-EC
10	10.96	C ₂₁ H ₂₁ O ₁₂ ⁺		465.1045	3.8	303	delphinidin-glycoside
11	11.67		C ₂₄ H ₃₄ O ₁₃	529.1926	2.0	377, 313, 161	globulisin A
12	11.67		C ₂₇ H ₃₆ O ₁₃	567.2087	2.6	326, 311	icariside E5
13	11.95	C ₂₁ H ₂₂ O ₁₁		449.1096	3.9	287, 151	eryodictiol-glycoside
14	11.95	C ₂₁ H ₂₀ O ₁₂		463.0889	3.8	301	quercetin-glycoside
15	12.21	C ₂₇ H ₃₀ O ₁₅		593.1519	3.0	285	kaempferol-rutinoside
16	12.32	C ₂₈ H ₃₂ O ₁₆		623.1617	1.7	315	isorhamnetin-rutinoside
17	12.58	C ₂₁ H ₂₀ O ₁₁		447.0936	3.1	285	kampferol-glycoside
18	12.89	C ₂₂ H ₂₂ O ₁₂		477.1042	3.0	315	isorhamnetin-glycoside
19	13.14	C ₃₀ H ₂₃ O ₁₂		575.1205	3.6	271	EC-a-EC
20	13.15	C ₁₅ H ₁₂ O ₅		271.0613	4.3	243, 191	naringenin
21	13.15	C ₂₁ H ₂₂ O ₁₀		433.1140	2.6	271	prunin
22	13.84	C ₉ H ₁₆ O ₄		187.0968	1.8	125, 97	azelaic acid
23	13.97		C ₂₇ H ₄₂ O ₁₂	557.2609	–1.9	511, 349	amygdalin
24	16.11	C ₁₅ H ₁₀ O ₇		301.0357	3.9	151, 121	quercetin
25	17.01	C ₁₈ H ₃₂ O ₅		327.2176	3.2	229, 199, 171	9,12,13-TriHOME (10,15)
26	17.92	C ₁₈ H ₃₄ O ₅		329.2331	2.7	311, 293, 229, 171	9,12,13-TriHOME (10)
27	18.61	C ₃₀ H ₄₈ O ₆		503.3383	3.2	305, 175	19α-hydroxyasiatic acid
28	22.96	C ₂₁ H ₃₉ O ₇ P		433.2361	2.7	279, 153	l-PA (18:2)
29	23.71	C ₁₈ H ₃₄ O ₄		313.2386	1.2	295, 277, 213, 183	12,13-DiHOME (9)
30	24.36	C ₂₁ H ₃₉ O ₇ P		433.2360	1.1	415, 279, 153, 135	l-PA (18:2)
31	24.64		C ₂₇ H ₅₂ O ₉ NP	564.3308	1.2	504, 279, 242, 184, 153	l-PC (18:2)
32	25.11		C ₂₇ H ₅₂ O ₉ NP	564.3303	0.7	504, 279, 242, 184, 153	l-PC (18:2)
33	25.73	C ₁₈ H ₃₆ O ₄		315.2537	0.8	297, 279, 201, 171	9,10-DHSA
34	26.34	C ₂₅ H ₅₂ O ₉ NP		540.3306	1.0	480, 255, 224, 184	l-PC (16:0)
35	26.70	C ₂₁ H ₃₉ O ₇ P		433.2360	1.0	415, 279, 153, 135	l-PA (18:2)
36	26.70		C ₂₇ H ₅₄ O ₉ NP	566.3464	1.2	506, 281, 242, 184	l-PC (18:1)
37	27.27		C ₂₇ H ₅₄ O ₉ NP	566.3461	0.9	506, 281, 242, 184	l-PC (18:1)
38	27.45	C ₁₈ H ₃₂ O ₃		295.2277	1.0	277, 233, 195, 99	13-HODE (9,11)
39	28.41	C ₂₂ H ₄₅ O ₉ P		483.2729	1.2	391, 255, 153	l-PG (16:0)
40	28.78	C ₁₈ H ₃₅ O ₃		297.2432	0.8	279, 251, 211, 197	12-HOME (9)

Abbreviations: EA: (epi)afzelechin; B: B-type linkage; EC: (epi)catechin; TriHODE: Tri-HydroxyOctadec-DiEnoic acid; TriHOME: Tri-HydroxyOctadec-MonoEnoic acid; l-PA: lyso-phosphatidic acid; DHSA: DiHydroxyStearic Acid; l-PC: lyso-phosphatidylcholine; l-PG: lyso-phosphatidylglycerol.

skin and enriched bread (control, 5-ASP, and 10-ASP), already subjected to photothermal stress, were extracted using ultrasound-assisted extraction in hydroalcoholic ethanol solution (EtOH/H₂O 80:20) in a 1:3 ratio (sample:solvent) (3 cycles, ultrasonic frequency of 35 kHz) in a water bath (Branson 5200, Milan, Italy) at room temperature for 30 min. Before the analysis, the samples were filtered through a polytetrafluoroethylene (PTFE) 0.45 μm Millipore filter (BGB Technology Inc., VA, USA) and freeze-dried.

2.10. Total phenols (TPC) and flavonoids (TFC) content in almond skin Treccina bakery product

The evaluation of total phenol content (TPC) was done following the procedure previously described by Loizzo et al. [14]. The TPC was determined spectrophotometrically at λ = 750 nm and expressed as mg gallic acid equivalent (GAE)/g extract. For the evaluation of the total flavonoid content (TFC) the methodology that used flavonoid-aluminum complex was assessed [34]. The TFC quantification was done spectrophotometrically at 510 nm, and result was expressed as mg quercetin equivalents (QE)/g extract.

2.11. Evolution of TPC and TFC in samples subjected to photothermal degradation process

Mathematic kinetic model is a very useful technique for investigation the impact of processing on food quality. The first order degradation

kinetic was applied following the equations:

$$-\ln(C_t/C_0) = kt \quad (1)$$

$$t^{1/2} = \ln(2)/k \quad (2)$$

where C₀ is the initial TPC or TFC concentration and C_t is the concentration of TPC and TFC after 3, 6, 9 days of photothermal stress [35].

2.12. Evaluation of Treccina bakery product antioxidant potential

The antioxidant activity of Treccina bakery product was assessed using different methods such as 2,2-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), 1,1-diphenyl-2-picrylhydrazyl (DPPH), and β-carotene bleaching test as previously described [14]. Ascorbic acid was used as the positive control in both assays. For β-carotene bleaching test a solution of Tween 20, β-carotene, linoleic acid, and sample (at concentration from 100 to 5 μg/mL) was prepared. After 30 min incubation at 45 °C the absorbance was read at λ = 470 nm [14]. Propyl gallate was used as a positive control. Results were expressed as inhibitory concentration 50% (IC₅₀).

2.13. Determination of inhibitory activity of enzymes linked to MeTs

To evaluate the hypoglycemic effects of Treccina sample, α-amylase, and α-glucosidase inhibitory activity will be assessed [14] whereas lipase inhibitory activity test will be applied to investigate the potential

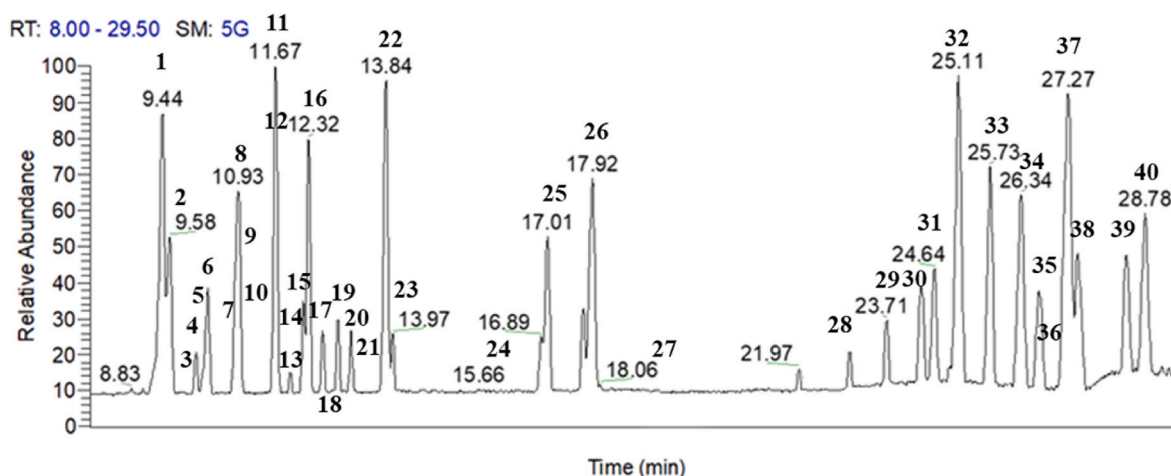


Fig. 1. UHPLC-HRMSMS profile, in negative mode, of EtOH extract of “Tuono” cultivar almond skins.

application of extracts as anti-obesity agents [36]. Results were expressed as inhibitory concentration 50% (IC_{50}).

2.14. Statistical analysis

Microsoft Excel 2010 software (Microsoft Corporation, Redmond, WA, USA) was used to calculate linear regression, repeatability assessment, average calculation, relative standard deviation (SD), and Pearson's correlation coefficient (r). Prism GraphPad Prism version 4.0 (San Diego, CA, USA) was used to calculate the concentration-response curve and the inhibitory concentration 50% (IC_{50}). The results were expressed as means of three different experiments \pm SD.

All data were statistically analysed by one-way variance analysis (ANOVA) using XLStat software version 7.5.2 for Microsoft Excel (Addinsoft, New York, NY, USA); the model included the effects of bread shape and ASP addition. For each analysis the model included three technical repeats for two independent experiments. Significant differences were calculated according to Tukey's multiple range tests. Differences at $**p < 0.01$ and $*p < 0.05$ were statistically significant.

3. Results and discussion

3.1. Chemical analysis

3.1.1. UHPLC-HRMSMS analysis of polar extract of “Tuono” almond skin

Hyphenated techniques play increasingly important roles in supporting phytochemical investigations. Specifically, UHPLC-HRMSMS is considered a powerful tool for profiling plant extracts [37]. In this study, a deep understanding of the chemical composition of EtOH extract and an exploration on the potential use of by-products as a source of bioactive compounds were performed. To achieve this, an analytical approach based on UHPLC-Q-Orbitrap, which combines high-performance liquid chromatography with a Q-Exactive hybrid quadrupole-Orbitrap mass spectrometer was applied. Previously, an LC-MS analysis on an EtOH extract from *P. dulcis* skin cultivar “Casteltermini” was conducted. This analysis revealed the presence of compounds primarily belonging to the flavonoid, anthocyanin, and oxylipin classes [14].

Herein, an analytical approach based on UHPLC-HRMSMS was carried out to investigate the primary and specialized metabolites present in the EtOH extract of *P. dulcis* skins cultivar “Tuono”. According to their accurate mass, characteristic fragmentation pattern, retention time, and existing literature data, 40 compounds (Table 2,) that correspond to specialized metabolites and polar lipid derivatives were tentatively identified (Fig. 1). Among these compounds, flavonoids constitute one of the most abundant classes. Specifically: flavan-3-ol monomers,

including catechin (1) and epicatechin (3); dimers (5, 8, 9, 19); oligomers (proanthocyanidins) (2 and 4); the well-known flavonol quercetin (24) and its glycosylated derivatives, kaempferol and isorhamnetin (14–18); flavanones, including eryodictiol-glycoside (13), naringenin (20), and prunin (21); anthocyanins, specifically cyanidin-glycoside (6) and delphinidin-glycoside (10). Additionally, we detected the presence of: icaricide E5 (12), a stilbene glucoside; and 19 α -hydroxyasiatic acid (27), a triterpenoid derivative. Notably, these compounds were previously reported in the almond skin of cultivar “Casteltermini” by Loizzo et al. [14]. Moreover, UHPLC-HRMSMS profiling showed the occurrence of azelaic acid (22), a nonanedioic acid, attributed by analysis of MS/MS spectra [38] and reported here for the first time in *P. dulcis* skins.

The careful analysis of UHPLC-HRMSMS profiling of the analysed skins extract revealed two peaks ascribable to cyanogenic glucosides. Specifically, prunasin (7), previously reported in *P. dulcis* seeds [12], was detected in almond skin for the first time. In detail, prunasin (7), identified as a formiate adduct, exhibited a precursor ion $[M-H + HCOOH]^-$ at m/z 340.1037. In the MS/MS spectrum, a fragment ion at m/z 162 corresponded to the dehydrated glucose ion, resulting from the loss of the mandelonitrile moiety [12]. Furthermore, UHPLC-HRMSMS analysis revealed a precursor ion $[(M + HCOOH)-H]^-$ at m/z 557.2609. Fragment ions at m/z 511, attributed to the loss of formic acid, and at m/z 349, originating from the further loss of a dehydrated hexose moiety, were associated with amygdalin (23). 1. Notably, amygdalin had been previously identified in the almond skin of the *P. dulcis* cultivar “Casteltermini”.

Finally, compound 11 was identified as globulisin A, a galloyl derivative of 2-hydroxy-1,8-cineol-2-O-glucopyranoside. In particular, compound 11 was detected as a formiate adduct, with a precursor ion $[(M + HCOOH)-H]^-$ at m/z 529.1926. During MS/MS analysis, compound 11 exhibited a product ion at m/z 377, resulting from the loss of the galloyl moiety (152 Da), and another product ion at m/z 313, attributed to the loss of the monoterpene moiety (170 Da). These findings align with the observations reported by Boulekbache-Makhlouf et al. [39]. Importantly, this study represents the first report documenting the occurrence of globulisin A in *P. dulcis*.

3.1.2. UHPLC-HRMSMS analysis of polar lipids occurring in “Tuono” almond skin

The accurate analysis of UHPLC-HRMSMS profiles in negative ion mode of the EtOH extract of “Tuono” almond skins showed the occurrence of polar lipids that were assigned, based on their accurate masses and characteristic fragmentation patterns, to oxylipins and phospholipids [40].

Peaks 25, 26, 29, 33, 38, and 40 displayed pseudomolecular ions characterized by a molecular formula $C_{18}H_{36-2n}O_{2m}$ with $n = 1, 2, 3$, or 4

Table 3
GC-MS analysis of “Tuono” almond skin *n*-hexane extract.

No.	Compounds ^a	Common name	KI ^b	KI ^c	A (%) ^d
1	Tetradecanoic acid	Myristic acid	1761	1764	1.1 ± 0.0
2	(<i>E</i>)-9-Hexadecenoic acid	Palmitoleic acid	1938	1936	0.5 ± 0.0
3	<i>n</i> -Hexadecanoic acid	Palmitic acid	1959	1964	10.9 ± 0.4
4	(<i>Z,Z</i>)-9,12-Octadecadienoic acid	Linoleic acid	2130	2134	35.5 ± 1.4
5	(<i>Z</i>)-9-Octadecanoic acid	Oleic acid	2145	2140	48.0 ± 1.9
6	<i>n</i> -Octadecanoic acid	Stearic acid	2172	2176	3.0 ± 0.1
Total composition					99.0 ± 3.8

^a Compounds are classified in order of linear retention time of the non-polar column (HP-5 MS).

^b Kovats' retention index (KI) on a HP-5 MS non-polar column.

^c Kovats' retention index (KI) reported for HP-5MS column reported in the literature (<https://webbook.nist.gov/>).

^d Area is the peak volume percentage of compound in the fixed oil sample. Results indicate mean values ± S.D. (standard deviation) of three determinations.

and $m = 1, 2, \text{ or } 3$ and a fragmentation pattern attributable to the class of oxylipins. These compounds are hydroxy fatty acids deriving from the oxidative metabolism of PUFAs such as linolenic acid (ALA, C18:3) and linoleic acid (LA, C18:2), differing in the unsaturation degree and number of hydroxyl groups [41]. Fragmentation patterns of oxylipins allowed us to define the position of hydroxyl groups and double bonds on the acyl chain. In detail, the MS/MS spectrum of compounds **25**, **26**, and **33** displayed a diagnostic fragment at m/z 171, corresponding to the shortened acyl chain having the carboxyl group as COO^- and an aldehyde as terminal group originating from the rearrangement of the hydroxyl function on C9, following the cleavage of the C9–C10 bond [40] (Table 2). Compound **29** displayed a different tandem mass spectrum with a characteristic peak at m/z 183, derived from neutral loss of 130 Da, corresponding to a molecule of hydroxylated heptanal that originated from the end-part of the acyl chain by the breakdown of the C11–C12 bond after the usual $\text{CHOH} \rightarrow \text{CHO}$ rearrangement involving the hydroxyl group at C12. Moreover, in the same way, the careful analysis of compounds **38** and **40** allowed us to assign these oxylipins as 13-HydroxyOctadec-Dienoic acid (9,11) (HODE) and 12-HydroxyOctadecMonoEnoic acid (**40**) (HOME), respectively [40]. Among identified oxylipins, only **25** and **26** were previously reported in the EtOH extract of the *P. dulcis* skin cultivar “Casteltermi” [14].

Table 4
Chemical parameters of control and ASP containing sweet doughs.

Samples	t_0					t_1				
	pH	TTA	D + L Lactic acid (mg/g)	Acetic acid (mg/g)	FQ	pH	TTA	D + L Lactic acid (mg/g)	Acetic acid (mg/g)	FQ
CTR	5.2 ± 0.0	6.6 ± 0.0	0.6 ± 0.1	0.1 ± 0.0	3.6	4.7 ± 0.0	7.6 ± 0.1	1.1 ± 0.2	0.2 ± 0.0	4.1
	b	a				b	a			
5-ASP	5.3 ± 0.0	6.2 ± 0.0	0.6 ± 0.1	0.1 ± 0.0	3.2	4.8 ± 0.0	7.4 ± 0.1	1.0 ± 0.2	0.2 ± 0.0	3.7
	a	b				a	b			
10-ASP	5.4 ± 0.1	5.9 ± 0.1	0.5 ± 0.1	0.1 ± 0.0	3.3	4.9 ± 0.0	7.1 ± 0.0	0.9 ± 0.1	0.2 ± 0.0	3.7
	a	c				a	c			
Significance	**	***	n.s.	n.s.	n.	***	***	n.s.	n.s.	n.
						a.				a.

Results indicate mean values ± S.D. (standard deviation) of six determinations (carried out in three technical repeats for two independent experiments). Data within a column followed by different letters are significantly different according to Tukey's test. Symbols: ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$. Abbreviations: TTA, total titratable acidity expressed in mL NaOH 0.1 N/10 g; FQ, Fermentation Quotient (molar ratio between lactic and acetic acids); CTR, control dough; 5-ASP, experimental dough enriched with 5 % (w/w) of almond skin in powder (ASP); 10-ASP, experimental dough enriched with 10 % (w/w) of ASP; n.a., not analysed; n.s., not significant.

Compounds **31**, **32**, **34**, **36**, and **37** were characterized by a different fragmentation pattern showing a main peak formed by a neutral loss of 60 Da. This product ion could be ascribed to the neutral loss of 60 Da from $[(M + \text{HCOOH})-\text{H}]^+$ allowing us to identify these compounds as lyso-phosphatidylcholine (l-PC) derivatives. This product ion could be attributed to the $[(M - 15)-\text{H}]^+$ ion, in which the l-PC derivative lost a methyl group from the choline head group to generate formic acid methyl ester; moreover, the presence of the product ion at m/z 184, corresponding to the phosphocholine unit, confirmed the nature of compounds **31**, **32**, **34**, **36**, and **37** as lyso-forms of phosphatidylcholine (l-PC) [40] (Table 2).

UHPLC-HRMSMS analysis of peaks **28**, **30**, and **35** and their pattern of fragmentations, allowed us to assign these compounds as different isoforms of lyso-phosphatidic acid 18:2 (l-PA 18:2) as suggested by product ions at m/z 279 and 153, ascribable to fatty acid 18:2 and mono-dehydrated glycerophosphate, respectively. Finally, peak **39** was assigned as lyso-phosphatidylglycerol 16:0 (l-PG 16:0) as suggested by the product ion at m/z 391 corresponding to the monodehydrated glycerophosphoglycerol anion [40]. To the best of our knowledge, this is the first report of phospholipids in *P. dulcis* skins (Table 2).

3.2. GC-MS analysis of hexane extract of “Tuono” almond skin

GC-MS analysis identified the presence of six major fatty acids (Table 3). The most abundant compound was oleic acid, constituting 48.01 ± 1.87 % of the total fatty acids. Linoleic acid followed closely, accounting for 35.50 ± 1.42 %. To a lesser extent, palmitic acid was present at 10.87 ± 0.37 %. The almond peel also contained smaller amounts of other fatty acids such as myristic acid, palmitoleic acid, and stearic acid (Table 3). These organic compounds are commonly found in almond peels grown in Sicily, Spain and California [42]. Notably, a study by Saura-Calixto et al. [43] analysed the fatty acid profile of a mixture of almond skin from almond cultivars growing in Palma de Mallorca (Spain). In their analysis, they found that oleic (47.13%), linoleic (40.34%), and palmitic acids (7.53%) were the most abundant compounds, demonstrating a chemical composition very similar to our findings. However, significant differences emerge when comparing these data with the chromatographic results obtained from the fixed oil of the Casteltermi cultivar. The latter exhibited a fixed oil characterized mainly by linoleic acid ($63.19\% \pm 2.56\%$), moderate quantities of palmitic acid ($16.65\% \pm 1.32\%$), and lower quantities of oleic acid ($8.41\% \pm 0.21\%$), clearly distinguishing itself from the data reported by the present study.

3.3. Sourdough and sweet leavened dough acidification parameters

The sourdough starter exhibited a pH value of 3.82 ± 0.11 and a TTA

Table 5
Microbiological analysis of control and ASP containing sweet doughs.

Samples	Media					
	PCA		mMRS		YPD	
	t ₀	t ₁	t ₀	t ₁	t ₀	t ₁
CTR	7.3 ± 0.0	7.7 ± 0.1	7.3 ± 0.0	7.6 ± 0.1	7.2 ± 0.1	7.6 ± 0.4
5-ASP	7.4 ± 0.1	7.9 ± 0.1	7.2 ± 0.1	7.7 ± 0.1	7.3 ± 0.1	7.6 ± 0.1
10-ASP	7.5 ± 0.1	7.8 ± 0.1	7.3 ± 0.0	7.6 ± 0.0	7.2 ± 0.0	7.6 ± 0.1
Significance	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

Results indicate mean values ± S.D. (standard deviation) of six determinations (carried out in three technical repeats for two independent experiments). Data within a column followed by different letters are significantly different according to Tukey's test. ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$. Abbreviations: PCA, plate count agar; mMRS, modified de Man, Rogosa, and Sharpe agar; YPD, yeast extract peptone dextrose agar; CTR, control dough; 5-ASP, experimental dough enriched with 5 % (w/w) of almond skin in powder (ASP); 10-ASP, experimental dough enriched with 10 % (w/w) of ASP; n.s., not significant.

of 12.10 ± 0.14 mL NaOH 0.1 N. The concentration of D + L lactic acid was 4.82 ± 0.22 mg/g while that of acetic acid was 1.12 ± 0.15 mg/g. The resulting Fermentation Quotient, calculated as the molar ratio of lactic acid to acetic acid, (FQ = mol lactic acid/mol acetic acid) was estimated at 2.87. This value falls slightly higher than the range 2.0–2.7 which Hammes and Gänzle [44] indicated to exert a considerable effect on the sensory characteristics and shelf life of bread. However, Spicher [45] suggested a wider FQ range (1.5–4.0) that registers a positive influence on the aromatic and textural characteristics of breads due to the lactic and acetic acids generated by sourdough LAB. The sourdough starter was characterized by LAB levels of 8.9 ± 0.5 Log CFU/g and yeasts at 6.1 ± 0.4 Log CFU/g. Overall, the microbiological and physicochemical characteristics of the sourdough used as starter in this study are comparable to the average values found in traditional Italian

sweet-leavened products [46].

The results of physicochemical analyses conducted on sweet-leavened doughs are reported in Table 4. Initially, CTR dough, right after ingredient mixing, exhibited a pH of 5.22. Subsequently, the addition of ASP led to higher pH values in the other two trials. These variations were influenced by the inherent pH of ASP, which is higher than that of soft wheat flour [47]. Despite the relatively short fermentation period (approximately 1 h), the pH consistently decreased in all doughs. Notably, the most significant pH reduction occurred in the CTR dough. In contrast, the trend for TTA (total titratable acidity) was opposite. Initially, the average TTA value was 6.25 mL NaOH 0.1 N/10 g, but by the end of the acidification process, it had risen to 7.38 mL NaOH 0.1 N/10 g. Interestingly, even though almond by-products are known for their acidic content, the CTR dough exhibited the highest TTA values both at the beginning (6.58 mL NaOH 0.1 N/10 g) and the conclusion (7.65 mL NaOH 0.1 N/10 g) of the fermentation process.

During fermentation, the concentrations of D + L lactic acid and acetic acid increased across all trials. Notably, the CTR trial exhibited the highest concentration of D + L lactic acid, both at the beginning (0.64 mg/g) and at the end of fermentation (1.12 mg/g). In contrast, the concentration of acetic acid remained comparable among the various trials. Interestingly, despite the consistent increase in TTA, the pH decrease was less pronounced after 1 h of fermentation. This phenomenon can be attributed to acetic acid generation, which contributes to TTA without significantly altering pH [48]. Specifically, the molar ratio (FQ) between lactic acid and acetic acid was 4.15 for the CTR dough, slightly higher than the range associated with a positive impact of sourdough on final products. For all other sweet doughs, the FQs fell within the range of 1.5–4.0.

The sourdough used as a starter was characterized by 8.36 ± 0.30 Log CFU/g of TMM, 8.61 ± 0.18 Log CFU/g of LAB, and 6.64 ± 0.42 Log CFU/g of yeasts. Plate counts of sweet doughs, both with and without ASP, are detailed in Table 5. Initially, all doughs prepared according to Table 1 hosted 7.17–7.32 Log CFU/g of LAB immediately after sourdough inoculation. Subsequently, these levels increased to 7.57–7.68



Fig. 2. Typical Sicilian sweet-leavened products processed at industrial level with varying levels of powdered almond skin: A. Treccina; B. Bombolone; C. Cuore; D. Ondoppio; E. Papillon; F. Ciambellina; G. Cavalluccio.

Table 6

Quality attributes of the Sicilian bakery leavened products processed with the addition of almond skin in powder.

Baked goods	Weight loss (%)	Specific volume (cm ³ /g)	Crust color			Crumb color		
			L*	a*	b*	L*	a*	b*
Treccina								
CTR	15.6 ± 1.6 a	5.8 ± 0.5	65.6 ± 4.0 a	11.7 ± 2.4	36.6 ± 1.4 a	80.4 ± 2.2 a	-1.3 ± 0.3 c	14.5 ± 0.0 c
5-ASP	13.0 ± 1.2 ab	5.4 ± 0.3	58.9 ± 2.4 ab	11.9 ± 1.2	29.8 ± 1.2 b	66.9 ± 1.3 b	5.0 ± 0.3 b	18.1 ± 0.2 b
10-ASP	10.2 ± 0.9 b	5.1 ± 0.4	56.2 ± 1.6 b	12.5 ± 0.1	29.0 ± 0.3 b	59.9 ± 0.3 c	7.4 ± 0.1 a	19.5 ± 0.2 a
Significance	**	n.s.	*	n.s.	***	***	***	***
Bombolone								
CTR	12.0 ± 0.8 a	5.4 ± 0.7	66.0 ± 1.5 a	10.7 ± 0.9	34.1 ± 0.2 a	77.1 ± 3.0 a	-1.1 ± 0.1 c	12.6 ± 0.2 b
5-ASP	9.4 ± 1.4 ab	5.1 ± 0.4	61.1 ± 2.0 b	11.3 ± 1.0	30.4 ± 0.8 b	60.8 ± 1.4 b	5.1 ± 0.3 b	18.2 ± 0.6 a
10-ASP	7.5 ± 0.7 b	4.8 ± 0.5	56.9 ± 1.7 b	12.7 ± 0.8	28.9 ± 1.5 b	55.6 ± 1.7 b	7.6 ± 0.3 a	19.2 ± 0.3 a
Significance	**	n.s.	**	n.s.	**	***	***	***
Cuore								
CTR	11.8 ± 1.3 a	5.8 ± 0.4	62.1 ± 1.4 a	11.5 ± 0.8	34.4 ± 0.5 a	77.5 ± 1.1 a	-1.1 ± 0.1 c	13.6 ± 0.7 c
5-ASP	9.2 ± 0.8 b	5.4 ± 0.7	58.0 ± 1.8 b	12.5 ± 1.0	30.2 ± 0.5 b	63.2 ± 0.6 b	4.7 ± 0.3 b	17.4 ± 0.6 b
10-ASP	8.0 ± 0.4 b	5.1 ± 0.3	57.9 ± 1.2 b	12.6 ± 0.9	26.9 ± 0.8 c	59.7 ± 1.3 c	7.3 ± 0.0 a	19.58 ± 0.5 a
Significance	**	n.s.	*	n.s.	***	***	***	***
Undoppio								
CTR	13.9 ± 0.4 a	6.0 ± 0.4	63.1 ± 3.6 a	12.5 ± 0.6	36.4 ± 0.7 a	77.2 ± 0.8 a	-1.1 ± 0.1 c	13.8 ± 0.6 c
5-ASP	12.0 ± 0.3 b	5.5 ± 0.2	58.3 ± 1.6 ab	12.6 ± 1.9	30.5 ± 0.3 b	65.3 ± 1.1 b	4.9 ± 0.0 b	17.9 ± 0.3 b
10-ASP	9.2 ± 0.8 c	5.4 ± 0.3	53.9 ± 0.4 b	13.5 ± 0.2	29.0 ± 0.7 b	58.5 ± 2.1 c	7.4 ± 0.2 a	19.3 ± 0.3 a
Significance	***	n.s.	**	n.s.	***	***	***	***
Papillon								
CTR	12.1 ± 0.7 a	6.1 ± 0.3	59.5 ± 3.4	12.8 ± 1.3	35.0 ± 0.5 a	78.1 ± 0.5 a	-1.1 ± 0.1 c	12.8 ± 0.2 c
5-ASP	11.0 ± 1.1 ab	5.6 ± 0.3	54.6 ± 1.5	13.6 ± 1.5	29.5 ± 1.5 b	64.1 ± 2.1 b	5.1 ± 0.2 b	17.7 ± 0.5 b
10-ASP	9.2 ± 1.0 b	5.2 ± 0.4	54.3 ± 2.0	13.7 ± 0.3	27.8 ± 1.2 b	56.5 ± 1.6 c	7.7 ± 0.5 a	19.7 ± 0.6 a
Significance	*	n.s.	n.s.	n.s.	***	***	***	***
Ciambellina								
CTR	12.9 ± 1.4 a	6.3 ± 0.4	61.4 ± 5.1	12.0 ± 0.5	34.5 ± 0.5 a	76.3 ± 2.2 a	-1.1 ± 0.0 c	12.9 ± 0.7 b
5-ASP	10.7 ± 0.2 ab	6.1 ± 0.5	56.2 ± 1.4	12.6 ± 2.5	29.9 ± 0.9 b	63.5 ± 0.5 b	5.3 ± 0.1 b	18.2 ± 0.1 a
10-ASP	9.7 ± 1.1 b	5.3 ± 0.5	55.7 ± 1.0	13.1 ± 0.6	26.6 ± 0.2 c	58.1 ± 0.9 c	7.5 ± 0.1 a	19.1 ± 0.1 a
Significance	*	n.s.	n.s.	n.s.	***	***	***	***
Cavalluccio								
CTR	15.6 ± 0.4 a	5.7 ± 0.3	61.4 ± 1.6 a	12.4 ± 0.8	35.2 ± 0.8 a	76.4 ± 1.1 a	-1.0 ± 0.2 c	12.7 ± 0.4 b
5-ASP	12.1 ± 0.9 b	5.3 ± 0.4	55.6 ± 0.7 b	12.8 ± 0.7	29.9 ± 0.2 b	63.8 ± 2.2 b	4.9 ± 0.1 b	16.6 ± 1.9 a
10-ASP	10.0 ± 0.4 c	5.0 ± 0.3	54.3 ± 1.9 b	13.9 ± 0.3	27.7 ± 0.3 c	61.0 ± 1.4 b	7.3 ± 0.4 a	19.1 ± 0.1 a
Significance	***	n.s.	**	n.s.	***	***	***	***

Results indicate mean values ± S.D. (standard deviation) of six determinations (carried out in three technical repeats for two independent experiments). Data within a column followed by different letters are significantly different according to Tukey's test. ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$. Abbreviations: CTR, control dough; 5-ASP, experimental dough enriched with 5 % (w/w) of almond skin in powder (ASP); 10-ASP, experimental dough enriched with 10 % (w/w) of ASP; n.s., not significant.

Log CFU/g after fermentation. Interestingly, yeast levels remained almost comparable to those of LAB before and after fermentation. This finding can be attributed to the addition of baker's yeast, which contributed to the overall yeast population rather than relying solely on sourdough yeast development. In line with previous research by Gaglio et al. [13], our present work confirms the versatility of sourdough technology even in the presence of ASP. Notably, ASP did not negatively impact the development of LAB and yeasts in sweet doughs.

In terms of safety for raw materials and baked goods, neither Enterobacteriaceae family members nor total coliforms were detected in ASP or sweet doughs. Additionally, spore-forming aerobic bacteria were absent in the final baked products. These findings strongly suggest that almond skin in powder form is stable and safe as a food ingredient. It is crucial that agri-food by-products must exhibit high hygienic quality to be effectively transformed from waste into valuable food matrices [49, 50]. In this context, ASP represents a profitable side production for almond facilities, contributing to both sustainability and safety.

3.4. Quality attributes of the final baked products

The main quality characteristics (weight loss, specific volume, firmness, and color) of the seven Sicilian sweet-leavened products (Treccina, Bombolone, Cuore, Undoppio, Papillon, Ciambellina, and Cavalluccio) processed in this study with 5 and 10 % (w/w) ASP (Fig. 2)

are reported in Table 6 and Fig. 3.

When incorporating ASP (almond skin powder) into sweet baked goods production, a decrease in weight loss and specific volume was observed across all seven sweet products in this study. Notably, this reduction was directly proportional to the percentage of ASP added. These findings align with similar results obtained when ASP was used in bread making [13] and biscuit production [18]. Pasqualone et al. [18] shed light on the reduction in weight loss observed in biscuits processed with ASP. They attributed this effect to the hygroscopicity of the fibers present in this by-product, which effectively limited water migration during baking. Additionally, the shape of the baked goods consistently influenced weight loss, particularly in terms of specific volume. Among the three trials considered (CTR, 5-ASP, and 10-ASP), the products with the highest weight loss values were Treccina and Cavalluccio, followed by Undoppio. Among the sweet baked goods studied, Undoppio, Papillon, and Ciambellina exhibited the highest specific volumes. However, an interesting contrast emerged: the firmness of these products increased with the addition of ASP (Fig. 3). This phenomenon can be attributed to the presence of ASP fibers. Dietary fibers from by-products play a crucial role in determining the hardness of baked goods [51]. Notably, the highest firmness value (0.01401 N/mm²) was recorded for the 10-ASP Treccina. In comparison, within the CTR trials, the morphogeometric parameter values varied significantly, ranging from 0.00717 for Papillon to 0.01107 for Cavalluccio.

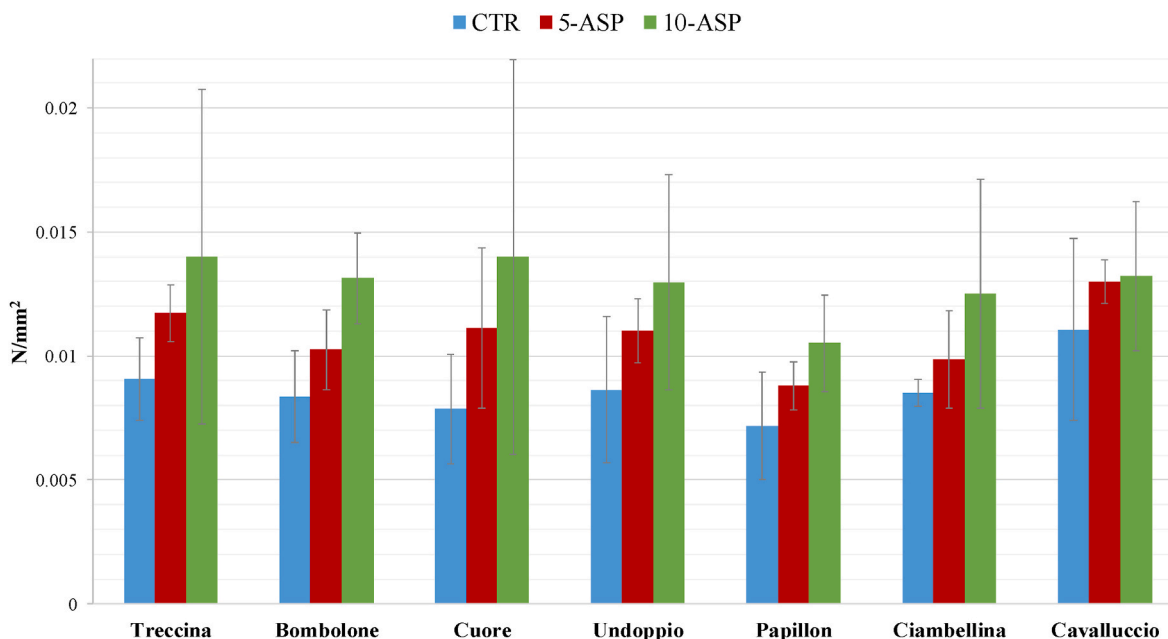


Fig. 3. Firmness of the Sicilian bakery leavened products processed with the addition of almond skin in powder. Abbreviations: CTR, control dough; 5-ASP, experimental dough enriched with 5 % (w/w) of almond skin in powder (ASP); 10-ASP, experimental dough enriched with 10 % (w/w) of ASP.

The addition of ASP significantly impacted the color of both sections (crust and crumb) in all the final sweet baked products analysed. L^* parameter of the crust was particularly influenced by ASP; it decreased from an average value of 77.72 for the CTR trials to 63.92 for 5-ASP trials and 58.47 for 10-ASP trials. The differences were less pronounced for L^* values recorded for the crumb of the products, going from 62.66 of CTR trials to 57.54 and 55.60 for 5-ASP and 10-ASP trials, respectively. Generally, a^* values increased in crust and, more consistently, in crumb with the addition of ASP, while b^* value behaved differently for crumb and crust; in particular, it decreased for crust and increased for crumb. The differences between crumb and crust color after addition of ingredients rich in fibres could be due to a stronger Maillard reaction for the crust [52]. The increase of fibre percentage determines a darker color (browning) of the crust of baked products [53, 54].

3.5. Image analysis of crumb structure

Crumb structure was studied using digitalized images of the baked good slices. The addition of ASP significantly influenced the crumb structure of the final sweet-leavened products (Table 7). The inclusion of ASP led to a reduction in mean cell area and an increase in cell density across all the investigated sweet-leavened products. As an example, Fig. 4 showcases the digital images and relative binary images of the Treccina trials. Interestingly, ASP did not interfere with cell formation during mixing. Instead, it enhanced cell density. However, this trend appears to be in contrast to the specific volume decrease (Table 6). Gaglio et al. [13] also observed a similar behavior in crumb parameters when processing breads using sourdough technology in the presence of ASP. These results align with previous findings: the addition of *Rubus idaeus* seed powder similarly increased cell density and void fraction while decreasing mean cell area in breads produced via sourdough fermentation [55]. Rubel et al. [54] Additionally, Rubel et al. [54] reported that changes in crumb structure parameters depend on the percentage of fibre enrichment, as seen with inulin-rich carbohydrate powder extracted from Jerusalem artichoke tubers or chicory.

3.6. Sensory evaluation and visual preference

The inclusion of ASP in the production of the sweet baked goods did not significantly alter the final products (Fig. 5). However, several attributes distinguished the control production from the trials conducted in the presence of ASP. The most noticeable difference was in crust and crumb color. In the presence of ASP, both internal and external sections of the baked goods exhibited a darker hue, with intensity increasing as the ASP percentage rose. Porosity, alveolation, and alveolation regularity were also affected by ASP addition, leading to a decreasing trend. ASP intensified the roasted odor while diminishing the yeasty odor and, particularly, the vanilla odor. The CTR trial received the highest scores for sweet taste, overall flavor, springiness, and chewiness. Interestingly, it also had the lowest scores for hardness. Previous investigations involving the addition of ASP to unleavened sweet products (biscuits) demonstrated consumer acceptability [18]. Additionally, in leavened products, such as sourdough breads Gaglio et al. [13], the inclusion of ASP led to a positive overall assessment by judges, even though the evaluation was limited to visual, texture, and odor sensations.

After conducting a descriptive analysis, a preference test was carried out—a crucial step when launching new food products, especially those derived from agri-food by-products or waste materials. In this study, the seven different baked products produced with ASP (almond skin powder) were evaluated by a panel of 87 untrained judges (Fig. 6). The results were clear: Treccina emerged as the preferred choice, scoring an impressive 8.65. The remaining products received preference scores within the range of 5.95–6.40. While the launch of ASP-containing baked goods other than Treccina might not be particularly risky, this second stage of sensory evaluation robustly indicates the potential consumer preference for Treccina over the other products. In summary, preference tests for novel food products are not only essential for better discrimination but also crucial for obtaining reliable and robust preference insights [56].

3.7. Total phenols and flavonoids content in almond skin enriched Treccina brioche

In our study we have quantified the TPC in Treccina and enriched Treccina samples as soon as it is produced (day 0), and after a certain

Table 7

Digital image analysis of crumb structure of the Sicilian bakery leavened products processed with the addition of almond skin in powder.

Baked goods	Void fraction (%)	Cell density (n cm ⁻²)	Mean cell area (mm ²)
Treccina			
CTR	35.1 ± 1.9 b	51.7 ± 2.0	0.7 ± 0.2
5-ASP	41.6 ± 2.3 a	60.6 ± 10.4	0.7 ± 0.1
10-ASP	42.5 ± 2.1 a	74.5 ± 15.3	0.6 ± 0.2
Significance	*	n.s.	n.s.
Bombolone			
CTR	37.7 ± 6.3	54.4 ± 1.7 b	0.7 ± 0.1
5-ASP	38.6 ± 7.1	67.8 ± 1.7 a	0.6 ± 0.0
10-ASP	40.1 ± 3.3	73.2 ± 5.0 a	0.5 ± 0.1
Significance	n.s.	***	n.s.
Cuore			
CTR	36.0 ± 2.2	53.2 ± 9.4	0.7 ± 0.2
5-ASP	38.0 ± 1.5	59.8 ± 9.1	0.6 ± 0.1
10-ASP	38.5 ± 4.4	67.6 ± 10.8	0.6 ± 0.1
Significance	n.s.	n.s.	n.s.
Undoppio			
CTR	37.5 ± 1.9 b	53.8 ± 1.9 b	0.8 ± 0.1 a
5-ASP	40.7 ± 3.2 ab	64.1 ± 8.8 ab	0.6 ± 0.0 ab
10-ASP	43.5 ± 1.2 a	69.3 ± 3.5 a	0.6 ± 0.1 b
Significance	*	*	*
Papillon			
CTR	41.1 ± 6.3	65.9 ± 6.7	0.6 ± 0.0
5-ASP	41.8 ± 1.0	68.7 ± 14.8	0.6 ± 0.1
10-ASP	43.1 ± 2.0	69.9 ± 8.3	0.6 ± 0.1
Significance	n.s.	n.s.	n.s.
Ciambellina			
CTR	31.6 ± 1.8 b	42.2 ± 0.4 b	0.7 ± 0.0
5-ASP	40.8 ± 4.0 a	64.9 ± 7.5 ab	0.6 ± 0.1
10-ASP	41.7 ± 2.8 a	77.6 ± 16.5 a	0.5 ± 0.2
Significance	*	*	n.s.
Cavalluccio			
CTR	35.2 ± 1.4	50.5 ± 9.8	0.7 ± 0.1
5-ASP	36.6 ± 2.7	62.4 ± 6.0	0.6 ± 0.1
10-ASP	38.7 ± 1.3	66.4 ± 10.2	0.6 ± 0.1
Significance	n.s.	n.s.	n.s.

Results indicate mean values ± S.D. (standard deviation) of six determinations (carried out in three technical repeats for two independent experiments). Data within a column followed by different letters are significantly different according to Tukey's test. ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$. Abbreviations: CTR, control dough; 5-ASP, experimental dough enriched with 5% (w/w) of almond skin in powder (ASP); 10-ASP, experimental dough enriched with 10% (w/w) of ASP; n.s., not significant.

number of days of photothermal stress (3, 6, 9 days). It is well known from the literature that the TPC is strictly influenced by several factors including almond variety, extraction procedure and data analysis [57, 58]. Table 8 revealed that TPC decreases after photothermal stress is application in both Treccina, and enriched Treccina samples (5- and 10-ASP). In fact, this value reducing from 85.6 to 58.8 mg GAE/g extract for leavened Treccina product on day 0 and day 9, respectively with a reduction in terms of percentage of -31.4%. Both enriched Treccina samples enriched with almond skin (5- and 10-ASP) showed an increase in the initial TPC value, proportional to the addition carried out. However, even in this case we observed a drastic reduction in TPC after 9 days with a value of -30.3% compared to the initial value in the 10-ASP sample.

A great variability in almond skin TPC was reported in literature. Bread functionalised with green almond skin powder displayed a TPC higher (~7-fold) than that of the control [59]. The enrichment of bread with almond skin from "Tuono" variety resulted in a TPC of 0.51, 0.73 and 0.88 mg GAE/g for semolina, 5%, and 10% almond skin enriched bread [13]. Previously, Garrido et al. [60] investigated the TPC in different American and Spanish almond skin and found values from 0.91 to 3.21 g/100 g. A similar trend was observed also in TFC where Treccina sample showed a TPC of 26.8 mg QE/g extract whereas values of 37.4 and 40.3 were recorded for 5-ASP, and 10-ASP, respectively. Also, in this case photothermal degradation determined a reduction of -14.9

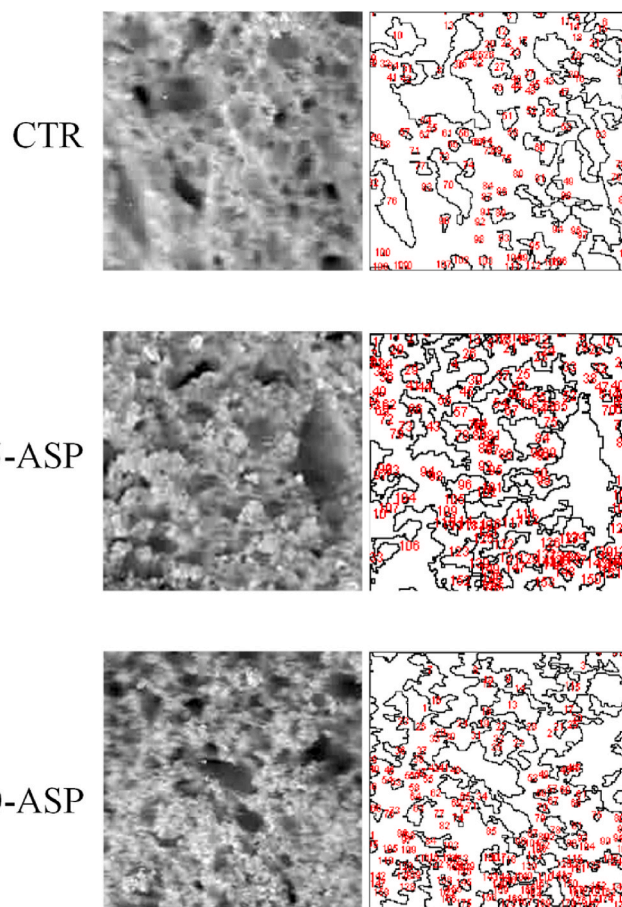


Fig. 4. Digital images (15 × 15 mm crumb area) converted to grey-level image (8 bit) of Treccina baked goods obtained without almond skin in powder (ASP) (CTR trial), with 5% (w/w) ASP (5-ASP trial), and 10% (w/w) ASP (10-ASP trial) and relative binary images obtained applying the Otsu's threshold algorithm in order to calculate void fraction, cell density, and mean cell area

% for control, and -17.8 and -15.2% for 5-ASP, and 10-ASP, respectively. Our values agree with those reported by Loizzo et al. [14] that found a TFC 20.38 mg QE/g extract in *Prunus dulcis* cv. Casteltermini EtOH extract.

3.8. Degradation kinetic of TPC and TFC as consequence of photothermal degradation

Kinetic modeling is currently applied to explain and predict the change in product quality as consequence of photothermal degradation process used to used mimic the effect of conservation over time. In our case the degradation kinetics of quantified bioactive compounds (TPC, and TFC) was done (Table 9). The kinetic rate (k) constant is an indicator that predicts the degradation of phytochemical content, where the lowest k value indicates better stability of phytochemicals. The values of half-life time ($t_{1/2}$) allow us to predict the progress of the degradation of these phytochemicals during storage. The first-order kinetic model was appropriate to monitor the effect of the application of photothermal degradation process on Treccina and enriched Treccina samples (5-ASP, and 10-ASP) with R^2 ranging from 0.9051 to 0.9894, and from 0.9572 to 1 for TPC and TFC, respectively (Table 9). Moreover, from analysis of data it is possible to observe as the addition of almond skin retard the half-life time of phytochemicals with TPC $t_{1/2}$ from 17.11475 days to 18.00382 days, and with TFC $t_{1/2}$ from 39.83604 days to 52.51115 for CTR and 10-ASP, respectively. All this demonstrates that the addition of almond skin improves the health potential of the product over time.

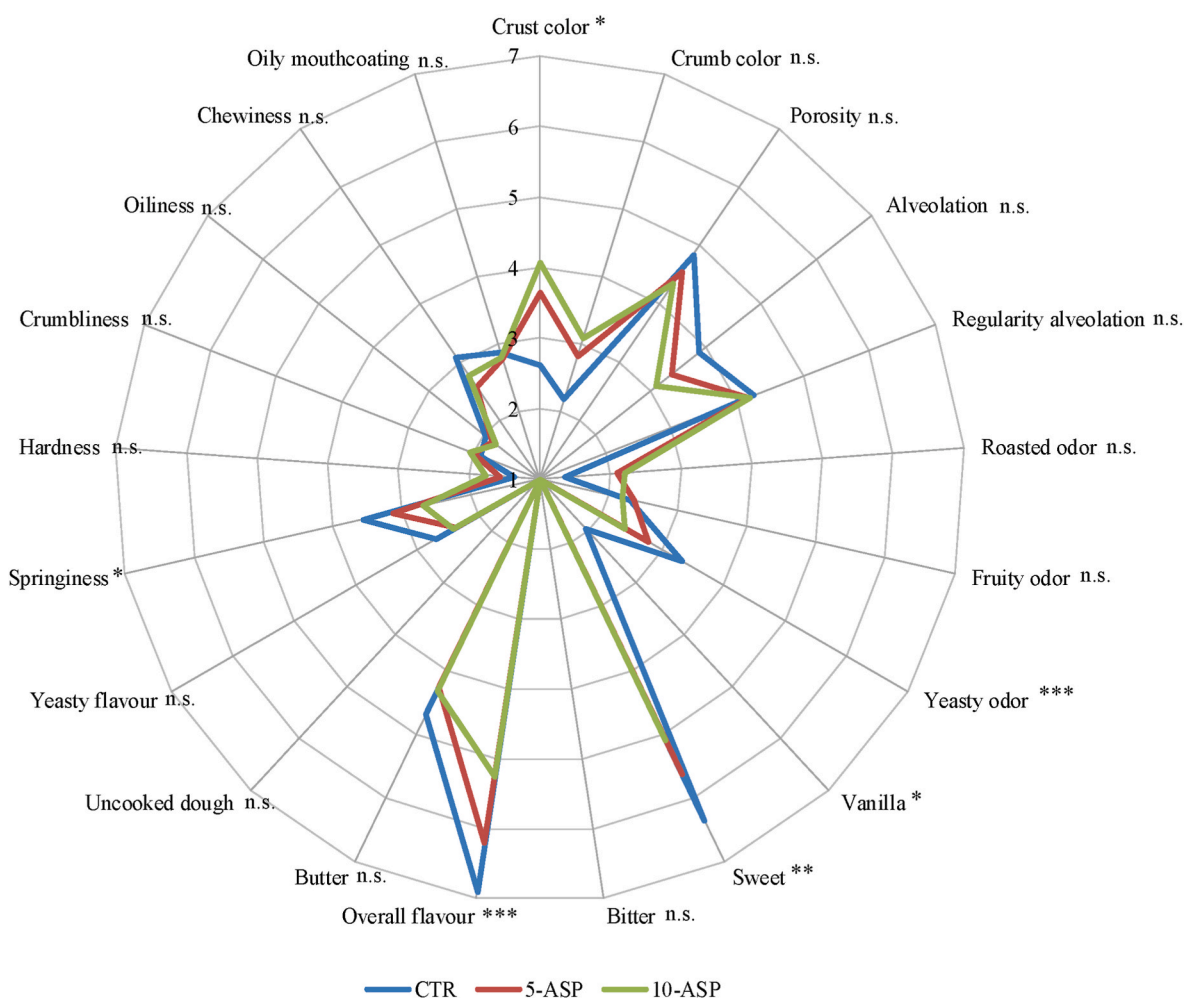


Fig. 5. Spider diagrams of descriptive sensory analysis of sweet-leavened products containing different percentages of powdered almond skin. Abbreviations: CTR. control baked goods; 5-ASP. experimental baked goods containing 5 % (w/w) of almond skin in powder (ASP); 10-ASP. experimental baked goods containing 10 % (w/w) of ASP; ***, $P < 0.001$; **, $P < 0.01$; *, $P < 0.05$.

3.9. Antioxidant activity of almond skin enriched Treccina photothermally aged

The effect of almond skin enrichment on radical scavenging activity of Treccina samples subjected to photothermal aging (CTR, 5-ASP, and 10-ASP) revealed that, independently by the applied test a reduction after 9 days was observed. In general, ABTS radical was more sensible to the action than DPPH radical cation (Table 10). In DPPH test at day 0 the enrichment increases the antioxidant potential with IC_{50} values of 504.9, 465.9, and 389.7 $\mu\text{g/mL}$ for CRT, 5-ASP, and 10-ASP, respectively. An IC_{50} value of 421.2 $\mu\text{g/mL}$ was recorded after 9 days of photothermal aging in 10-ASP. However, all these values are significant higher than those found for the positive control ascorbic acid (IC_{50} value of 5.0 $\mu\text{g/mL}$). A similar trend was observed also in ABTS test (Table 10). At day 9 samples exhibited IC_{50} values of 24.5, 20.1, and 18.6 $\mu\text{g/mL}$ for CRT, 5-ASP, and 10-ASP, respectively. Also in this case, although there is a degradation of the phytochemicals responsible for the antioxidant activity, the enrichment led to an improvement in the performance of the product.

No significant differences were recorded between control Treccina and enriched Treccina even at maximum addition of almond skin in the protection from lipid peroxidation monitored by using β -carotene bleaching test. Among enriched product, 10-ASP resulted the most active with IC_{50} values from 35.1 to 42.0 at day 0 and 9, respectively) (Table 10). Pearson's correlation coefficient highlights that phenols and

flavonoids are not the only compounds responsible for the bioactivity of the extracts since positive correlation were recorded only for DPPH with r value of 0.9 for both TPC and TFC, respectively. Our data agreed with those reported by Pasqualone et al. [18] that enriched biscuits with almond skin at 10 (AS10) and 20 % (AS20 %) on a wheat flour basis and obtained in the AS20, a DPPH radical scavenging activity ~ 5 -times higher than the control biscuit. A similar situation was observed, also by Gaglio et al. [13] where the antioxidant activity of functional bread is strictly dependent on the amount of almond skin added to the product. However, some differences have been found, with the same percentage added (8 %), in relation to the geographical origin of almonds [59].

3.10. Effect of almond skin enriched Treccina on enzymes linked with MetS

All samples exhibited inhibitory activity in a concentration-dependent manner. Furthermore, as we expected, the activity tends to decrease following the application of photothermal degradation over time. Indeed, CTR extract exhibited IC_{50} values of 275.8 and 289.2 $\mu\text{g/mL}$ against α -amylase, and 237.4 and 297.4 $\mu\text{g/mL}$ against α -glucosidase, respectively, both after 0 and 9 days of photothermal degradation (Table 11). Whereas, 10-ASP showed IC_{50} values of 189.8 and 178.9 $\mu\text{g/mL}$ against α -amylase, and α -glucosidase, respectively the day of the production (Table 11). Regarding pancreatic lipase, after 9 days of photothermal degradation IC_{50} values of 480.1, 400.2, and 375.5 $\mu\text{g/mL}$

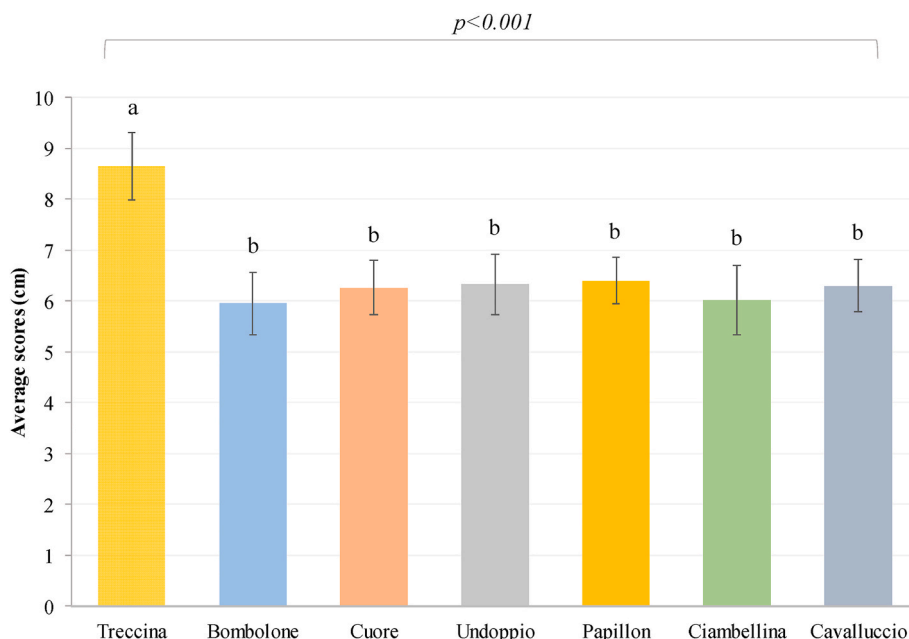


Fig. 6. Histogram representing consumers' preference towards the different sweet leavened products containing different percentages of powdered almond skin. Results indicate mean values \pm S.D. (standard deviation). Different superscript letters indicate statistically significant differences according to Tukey's test.

Table 8

TPC and TFC in Treccina bakery product submitted to different period of photothermal degradation.

TPC [^]	CTR	5-ASP	10-ASP	Sign.
0	85.6 \pm 3.5 cA	178.4 \pm 4.8 bA	186.8 \pm 4.8 aA	**
3	74.7 \pm 4.7 cB	148.3 \pm 6.9 bB	174.2 \pm 8.3 aB	**
6	68.5 \pm 2.8 cC	139.4 \pm 4.6 bC	162.5 \pm 4.8 aC	**
9	58.8 \pm 2.9 cD	112.3 \pm 7.9 bD	130.1 \pm 3.8 aD	**
Significance	**	**	**	**
TFC [^]	CTR	5-ASP	10-ASP	Sign.
0	26.8 \pm 1.2 cA	37.4 \pm 1.9 bA	40.3 \pm 3.7 aA	**
3	25.9 \pm 1.6 cB	34.6 \pm 1.9 bB	38.7 \pm 1.7 aB	**
6	24.1 \pm 2.8 cC	32.7 \pm 2.8 bC	37.5 \pm 2.6 aC	**
9	22.8 \pm 2.1 cD	30.8 \pm 2.6 bD	34.3 \pm 1.8 aD	**
Significance	**	**	**	**

CTR: Treccina; 5-ASP: Treccina enriched with 5 % almond skin powdered; 10-ASP: Treccina enriched with 10 % almond skin powdered."with "Abbreviations: CTR. control baked goods; 5-ASP. experimental baked goods containing 5 % (w/w) of almond skin in powder (ASP); 10-ASP. experimental baked goods containing 10 % (w/w) of ASP.

Table 9

First-order degradation kinetic parameters of TPC and TFC in Treccina, and almond skin enriched Treccina samples subjected to photothermal degradation process for several days (3, 6, and 9 days).

Samples	TPC			TFC		
	k (days ⁻¹)	t _{1/2} (days)	R ²	k (days ⁻¹)	t _{1/2} (days)	R ²
CTR	0.0405	17.11475	0.9894	0.0174	39.83604	0.9572
5-ASP	0.0483	14.35087	0.9624	0.0224	30.94407	0.9877
10-ASP	0.0385	18.00382	0.9051	0.0132	52.51115	1

CTR: Treccina; 5-ASP: Treccina enriched with 5 % almond skin powdered; 10-ASP: Treccina enriched with 10 % almond skin powdered."with "Abbreviations: CTR. control baked goods; 5-ASP. experimental baked goods containing 5 % (w/w) of almond skin in powder (ASP); 10-ASP. experimental baked goods containing 10 % (w/w) of ASP.

Table 10

Evaluation antioxidant potential of Treccina, and almond skin enriched Treccina samples subjected to photothermal degradation process for several days (3, 6, and 9 days).

DPPH	CTR (IC ₅₀ in μ g/mL)	5-ASP (IC ₅₀ in μ g/mL)	10-ASP (IC ₅₀ in μ g/mL)	Sign.
0	504.9 \pm 10.2 aD	465.9 \pm 9.6 bD	389.7 \pm 8.5 cD	**
3	520.4 \pm 10.7 aC	479.0 \pm 9.7 bC	395.9 \pm 8.7 cC	**
6	529.6 \pm 10.9 aB	490.3 \pm 9.5 bB	403.9 \pm 8.8 cB	**
9	545.8 \pm 11.0 aA	502.2 \pm 10.1 bA	421.2 \pm 9.8 cA	**
Significance	**	**	**	**
ABTS	CTR (IC ₅₀ in μ g/mL)	5-ASP (IC ₅₀ in μ g/mL)	10-ASP (IC ₅₀ in μ g/mL)	Sign.
0	9.7 \pm 0.1 cD	15.2 \pm 0.5 aD	14.3 \pm 0.2 bD	**
3	13.3 \pm 0.2 cC	18.1 \pm 0.9 aC	16.8 \pm 0.3 bC	**
6	18.8 \pm 0.4 bB	19.4 \pm 0.9 aB	17.2 \pm 0.3 cB	**
9	24.5 \pm 0.7 aA	20.1 \pm 0.4 bA	18.64 \pm 0.3 cA	**
Significance	**	**	**	**
β -Carotene bleaching test	CTR (IC ₅₀ in μ g/mL)	5-ASP (IC ₅₀ in μ g/mL)	10-ASP (IC ₅₀ in μ g/mL)	Sign.
0	30.4 \pm 1.8 cD	39.1 \pm 2.9 bD	35.1 \pm 1.5 aD	**
3	32.1 \pm 0.9 cC	40.2 \pm 2.9 bC	38.1 \pm 2.1 aC	**
6	34.7 \pm 2.6 cB	45.4 \pm 2.0 bB	40.4 \pm 3.0 aB	**
9	37.8 \pm 1.8 cA	46.9 \pm 3.0 bA	42.0 \pm 3.5 aA	**
Significance	**	**	**	**

CTR: Treccina; 5-ASP: Treccina enriched with 5 % almond skin powdered; 10-ASP: Treccina enriched with 10 % almond skin powdered."with "Abbreviations: CTR. control baked goods; 5-ASP. experimental baked goods containing 5 % (w/w) of almond skin in powder (ASP); 10-ASP. experimental baked goods containing 10 % (w/w) of ASP.

were recorded for CRT, 5-ASP, and 10-ASP, respectively (Table 11). Pearson's correlation coefficient demonstrated that both TPC and TFC are responsible of the enzymatic inhibitory activity. A more potent ability of almond skin extract to inhibit key enzymes involved in MetS was recently evidenced by Loizzo et al. [14] with another Sicilian

Table 11

Inhibition of key enzymes involved in MeTS by Treccina. and almond skin enriched Treccina samples subjected to photothermal degradation process for several days (2, 6, and 9 days).

α -Amylase	CTR (IC ₅₀ in μ g/mL)	5-ASP (IC ₅₀ in μ g/mL)	10-ASP (IC ₅₀ in μ g/mL)	Sign.
0	275.8 \pm 6.7 aD	232.4 \pm 5.7 bD	189.8 \pm 3.9 cD	**
3	279.7 \pm 7.3 aC	235.8 \pm 7.0 bC	190.2 \pm 3.1 cC	**
6	287.2 \pm 6.8 aB	240.9 \pm 4.9 bB	195.1 \pm 5.8 cB	**
9	289.2 \pm 6.2 aA	242.7 \pm 5.7 bA	198.2 \pm 6.3 cA	**
Significance	**	**	**	
α -Glucosidase	CTR (IC ₅₀ in μ g/mL)	5-ASP (IC ₅₀ in μ g/mL)	10-ASP (IC ₅₀ in μ g/mL)	Sign.
0	237.4 \pm 6.4 aD	204.1 \pm 7.5 bD	178.9 \pm 7.1 cD	**
3	245.9 \pm 8.7 aC	205.2 \pm 4.9 bC	184.2 \pm 8.1 cC	**
6	289.9 \pm 3.9 aB	207.1 \pm 7.1 bB	189.0 \pm 6.3 cB	**
9	297.4 \pm 5.8 aA	209.2 \pm 8.0 bA	190.2 \pm 7.3 cA	**
Significance	**	**	**	
Lipase	CTR (IC ₅₀ in μ g/mL)	5-ASP (IC ₅₀ in μ g/mL)	10-ASP (IC ₅₀ in μ g/mL)	Sign.
0	448.9 \pm 6.8 aD	369.6 \pm 5.8 bD	351.1 \pm 6.5 cD	**
3	453.8 \pm 11.3 aC	381.8 \pm 6.8 bC	362.8 \pm 3.9 cC	**
6	476.2 \pm 8.9 aB	385.7 \pm 7.5 bB	370.2 \pm 8.7 cB	**
9	480.1 \pm 10.6 aA	400.2 \pm 7.4 bA	375.5 \pm 9.3 cA	**
Significance	**	**	**	

CTR: Treccina; 5-ASP: Treccina enriched with 5 % almond skin powdered; 10-ASP: Treccina enriched with 10 % almond skin powdered." with "Abbreviations: CTR. control baked goods; 5-ASP. experimental baked goods containing 5 % (w/w) of almond skin in powder (ASP); 10-ASP. experimental baked goods containing 10 % (w/w) of ASP.

almond variety (*P. dulcis* cv. Casteltermini). Tsujita et al. [61] identified in highly polymerized polyphenols, isolated by *P. dulcis* skin, the compounds responsible for the powerful α -amylase inhibitory activity, which retard the absorption of carbohydrate.

4. Conclusions

The drive to repurpose W&BP has spurred the development of novel foods. In this study, the polyphenol-rich peel from almond skin was used to produce brioches with added value. This innovative ingredient underwent industrial-level processing, thorough chemical characterization, and transformation using sourdough and yeast fermentation technology. Microbiological safety was a priority. Fortunately, undesirable microorganisms, including spore-forming aerobic bacteria, members of the Enterobacteriaceae family, and total coliforms, were absent in both the ASP, the doughs, and the final brioches. The consumer response was overwhelmingly positive, with Treccina emerging as the preferred type among the final products. This sweet brioche is typically consumed as a snack or for breakfast in Sicily. The enrichment of Treccina with almond skin powder (10% w/w) resulted in a functional product characterized by a promising radical scavenging potential as well as protection from lipid peroxidation. Moreover, functionalised brioche was able to inhibit enzymes able to prevent hyperglycaemia and hyperlipidaemia that represent the common aspects of metabolic syndrome. These health properties were maintained even if Treccina brioches were subject to photothermal degradation process. The formulation of this enriched Treccina allow us to create a new functional sweet-leavened product with important link with the Sicilian territory, not only for the use of almond by-products but also for the formulation and traditional shape of the product which will make it easier to place on the market. In conclusion, this study provides further evidence on the valorisation of almond skin and shows a large margin of its exploitation in the sector of sweet leavened baked goods.

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CRedit authorship contribution statement

Giuliana Garofalo: Methodology, Investigation, Formal analysis. **Raimondo Gaglio:** Writing – original draft, Methodology, Conceptualization. **Enrico Viola:** Software, Formal analysis, Data curation. **Monica Rosa Loizzo:** Writing – original draft, Methodology. **Natale Badalamenti:** Writing – original draft, Formal analysis, Data curation. **Maurizio Bruno:** Writing – review & editing. **Francesco Sottile:** Resources, Funding acquisition. **Vincenzo Sicari:** Formal analysis, Data curation. **Antonietta Cerulli:** Writing – original draft, Data curation, Formal analysis. **Sonia Piacente:** Writing – review & editing. **Nicola Francesca:** Project administration. **Luca Settanni:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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