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Characterization and evaluation of antioxidant potential of onion peel extract of eight differentially pigmented short-day onion (*Allium cepa* L.) varieties

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Outer papery peel of onion bulb is an inevitable bio-waste generated in the course of postharvest handling and processing. Onion peels are rich source of nutraceutically important polyphenolic compounds having many therapeutic potentials. In this study, we characterized onion peel extract (OPE) of eight differentially pigmented short-day onion varieties through ultra-high-performance liquid chromatography coupled with high-resolution single stage Orbitrap spectrometry and evaluated the antioxidant potential. A total of 49 phenolic compounds were identified in this study which include 33 anthocyanin, 8 flavanol, 4 flavones, and 1 each of pyranoanthocyanin, chalcone, phenolic acid, and ellagitannins. Anthocyanin was the most abundant polyphenolic compound followed by flavanol in all the varieties. Among anthocyanin, 10 cyanidin, 10 delphinidin, 4 peonidin, 4 petunidin, 3 pelargonidin, and 2 malvidin were identified. Cyanidin-3-(6-malonylglucoside), delphinidin, and delphinidin-3-galactoside were the predominant pigment in dark red varieties (BDR and BRJ), and its abundance suggests a key role in the differential pigmentation pattern of onion peel. Total phenol content (TPC) in peels ranged from 1738.21 to 1757.76 mg GAE/100 g DW in dark red onion, 1306.58 to 1646.73 mg GAE/100 g DW in red onion, and 78.77 to 85.5 mg GAE/100 g DW in white onion varieties. The mean total anthocyanin content was maximum (28.23 mg/100 g DW) in dark red varieties (BDR) and minimum (0.11 mg/100 g DW) in white variety (BSW). Total antioxidant activity ranged from 4.71 to 79.80 $\mu\text{mol/g DW}$, 22.71 to 286.7 $\mu\text{mol/g DW}$, and 8.72 to 156.89 $\mu\text{mol/g DW}$ estimated through FRAP, ABTS, and DPPH methods, respectively. In all three methods, it was maximum in dark red var. BDR and minimum in white var. BSU.

KEYWORDS

antioxidant, anthocyanin, flavonoids, onion peel extract, quercetin

1 Introduction

Onions are among the earliest domesticated vegetables in human history and possess several health benefits due to their unique bioactive compounds (Elattar et al., 2024). However, the inconvenience of peeling and cutting fresh onions has led to a growing demand for ready-to-use onion products, such as dehydrated onions and minimally processed options such as

peeled or pre-cut onions (Gorrepati et al., 2014; Ahamad et al., 2024). Processing onions into various value-added products generates large amounts of bio-waste, primarily in the form of outer skins, peels, and basal and apical trimmings (Trigueros et al., 2024). Disposal of this waste is a major challenge for the industries as it has characteristic odor due to the presence of sulfur containing compounds (Chadorshabi et al., 2022). However, this waste can advantageously be used as a potential source for extraction of high-value secondary metabolites, development of functional/nutraceutical food, energy, and biogas production (Kumar et al., 2022; Stoica et al., 2022). Sagar et al. (2022) outline the methods for transforming onion waste into valuable biomolecules using a biorefinery approach to enhance the circular bioeconomy.

Onion skin extracts offer natural alternatives for preventing and treating diseases related to oxidative stress, microbial infections, or cancer (Bozinou et al., 2023). Onion peel extract (OPE) is reported to have antimicrobial (Sagar and Pareek, 2020a; Joković et al., 2024), antibacterial (Moosazad et al., 2019), antidiabetic (Jung et al., 2011; Vu et al., 2020), anti-obesity (Moon et al., 2013), anti-thrombotic (Lee et al., 2013), and anti-cancerous (Galavi et al., 2021) properties. OPE also decreases the level of total cholesterol, low-density lipoprotein, and atherogenic index (Kim et al., 2012). Onion peel extract is a promising component of future nutraceuticals and value-added products (Kim et al., 2013). Red onion skin can be used for producing value-added products as they are rich in bioactive compounds especially phenolics and flavonoids (Chadorshabi et al., 2022). Nutraceutical properties of onion peel have been augmented for the development of many value-added products such as wheat pasta (Michalak-Majewska et al., 2020), bread (Piechowiak et al., 2020), pizza (Sagar and Pareek, 2020b), and various meat products.

Onion peel contains wide array of polyphenolic compounds such as flavanols, anthocyanins, and tannins (Sharma et al., 2016; Suh et al., 1999). Ly et al. (2005) reported nine phenolic compounds in dry outer scales of onion (*Allium cepa* L.). The presence of ferulic, gallic, and protocatechuic acids, quercetin, and kaempferol was reported in extracts of red onion peel (Singh et al., 2009). Lee and Mitchell (2011) reported primary flavonoids in outer paper, first, and second layers of onion as quercetin 3,4-O-diglucoside, quercetin 3-O-glucoside, quercetin 4'-O-glucoside, isorhamnetin 4'-O-glucoside, and quercetin aglycone. Sagar et al. (2020) described the flavonoids, total phenols, and antioxidant properties of onion skin of 15 Indian cultivars. Anthocyanins are versatile natural pigment, widely described for nutraceutical properties associated with it. Anthocyanin-associated colors are mainly due to cationic flavylium ions (red), quinoidal bases (violet), and its colorless adducts (Fronsd et al., 2019). Onions with fascinating pigmentation patterns from dark red, yellow to white colors are globally produced. The abundance of phenolic compounds in the outer scales of onions is described to be associated not only with colors but also with many biochemical traits (Metrani et al., 2020). In general, the levels of flavanol are higher in yellow onions than red onions (Soininen et al., 2014). Sweet onion contains 2- to 3-fold higher isorhamnetin 4'-glucoside than red onion cultivars (Olsson et al., 2010). It has been reported that the antioxidant and anticancer properties of methanolic extracts from different parts (flesh and peel) of onion were significantly different in white, yellow, and red onion (Jeong et al., 2009). Sagar et al. (2021) studied the physicochemical and thermal characteristics of onion skin from 15 Indian cultivars for possible food applications and reported that the skin of cv. "NHRDF Red" was best source of protein, fiber, and minerals, suggesting its suitability for developing a food product.

Although ample amount of literature reports the pharmacological and nutraceutical potential of onion skin, most of the study is limited to profiling of few known compounds. Moreover, scanty information is available regarding short-day cultivars of onion which is of higher preference under subtropical Indian conditions. Mass spectrometry-based detections are highly sensitive and selective for identification. Therefore, we did high-resolution UHPLC-Orbitrap-Mass Spectrometry-based characterization of phenolic compounds and established putative relation with differential pigmentation in OPE of eight distinctly pigmented short-day onion cultivars ranging from dark red to white.

2 Materials and methods

2.1 Plant material






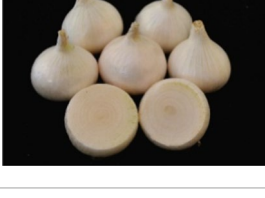
A field experiment was conducted during the winter season at the Indian Council of Agricultural Research-Directorate of Onion and Garlic Research (ICAR-DOGR) farm in Pune, Maharashtra, India. The site, located at 18.32° N and 73.51° E, is 645 m above sea level and has a tropical dry humid climate with an average annual precipitation of 820 mm. The soil at the site is clay loam, with low available nitrogen and medium soil organic carbon. The field experiment, designed as a completely randomized block design, included eight onion cultivars: Bhima Dark Red (BDR), Bhima Raj (BRJ), Bhima Super (BSR), Bhima Red (BRD), Bhima Shakti (BSK), Bhima Kiran (BKN), Bhima Shweta (BSW), and Bhima Shubra (BSU), each replicated three times (Table 1). Onion seeds were sown in the nursery in the second week of October. Organic manure was applied in the field at 5 t ha⁻¹ before transplanting. On the day of transplanting, the pre-emergence herbicide oxyfluorfen was applied, followed by irrigation for weed control. Before transplanting, 100% of the required phosphorus, potassium, and sulfur and 20% of nitrogen were applied as basal fertilizers (10:26:26, muriate of potash, and bentonite sulfur). Forty-five-day-old seedlings were transplanted in the third week of December at 15 cm spacing between rows and 10 cm between plants, maintaining a plant density of 66 plants m⁻² in 16.8 m² plots. The remaining 80% of nitrogen was applied through urea in 11 equal splits at 6-day intervals from 0 to 60 days after transplanting. Irrigation was provided via drip system, weeds were manually removed 45 days after transplanting, and other intercultural and plant protection practices followed ICAR-DOGR's guidelines. Onion bulbs were harvested in the second week of April, once 50% of the plants had top fall. After a 3-day field curing, bulbs were separated from the foliage, leaving a 2.5 cm neck. Leaves were removed and cured in farm shade for 2 weeks. The outer two papery layers of onion were removed from bulb, dried in shade, and powdered using kitchen blender. One part was used for LC-MS characterization at National Referral Laboratory, ICAR-National Research Centre for Grapes, Pune, and the remaining sample were used for biochemical analysis.

2.2 Characterization of phenolic compounds

2.2.1 Sample preparation

Dried onion peel powder (2 g) was preliminary soaked in 10 mL of water for 30 min followed by extraction with 10 mL of acidified methanol by continuous vortexing. Followed by extraction, the vial was centrifuged at 10,000 rpm for 10 min; the supernatant was taken,

TABLE 1 Details of onion varieties taken for the study.

Variety	Color category	Image
Bhima Dark Red (BDR)	Dark Red	
Bhima Raj (BRJ)		
Bhima Super (BSR)	Red	
Bhima Red (BRD)		
Bhima Shakti (BSK)		
Bhima Kiran (BKN)	Light Red	
Bhima Shweta (BSW)	White	
Bhima Shubra (BSU)		

diluted appropriately, and injected to UHPLC-Orbitrap MS for qualitative identification of anthocyanin and other major phenolic compounds.

2.2.2 LC-MS [UHPLC-Orbitrap MS] conditions

An Ultimate 3000-series Ultrahigh-Performance Liquid Chromatograph (UHPLC) hyphenated to a Q Exactive mass spectrometer (MS) (Thermo Fisher Scientific, Bremen, Germany) was used with an Ascentis Express C18 (100 × 2.1 mm, 2.7 μm) column (Supelco). The mobile phase comprised of (A): methanol: water (10:90) and (B): methanol: water (90:10) with 0.2% formic acid in both phases. The gradient program was 0–1 min/95% A, 1–5 min/95–55% A, 5–10 min/55–2% A, 10–14 min/2% A, 14–15 min/2–95% A, and 15–20 min/95% A, at 0.4 mL/min flow rate. A heated-electrospray ionization (H-ESI) source was used. The H-ESI parameters in positive polarity were as follows: sheath gas flow rate, 45; auxiliary gas flow rate, 8; sweep gas flow rate, 1; spray voltage, 3.50 kV; S-lens RF level, 50.0; capillary temperature, 320°C; S-lens RF level, 50.0; heater temperature, 300°C. The MS analysis was performed in full scan (70,000 full width at half maxima at m/z 200), followed by data-dependent MS/MS (ddMS2) at 17500 resolution (m/z 200) with stepped collision energy, operated at 18, 35, and 70 V maintaining the automatic gain control (AGC) target at 1e⁶.

2.2.3 Data processing

The LC-MS data files (*n* = 3, biological replications) were processed by the Trace finder software (version 3.3, Thermo Fisher Scientific). The automated data processing involved compound identifications by comparison with a database of anthocyanin, phenolic compounds, and their derivatives. This database comprised more than 235 compounds with compound specific information (molecular formula, adduct, monoisotopic molecular mass, and fragment mass) from various web-based resources (e.g., ChemSpider) and published research papers.

2.3 Determination of total anthocyanin content (TAC)

Total monomeric anthocyanin was determined based on the principle of pH-dependent structural changes from colored oxonium ion to colorless hemiketal forms (Lee et al., 2005) with some modifications suggested by Krithika et al. (2020). Each extract (200 μL) was diluted separately with 800 μL of 0.025 M potassium chloride buffer (pH 1.0) and 0.4 M sodium acetate buffer (pH 4.5) and incubated for 15 min in dark. Absorbance for each dilution was taken using SpectroStar Nano plate (BMG Labtech) at 520 and 700 nm against blank made of distilled water. Total anthocyanin content was expressed as cyanidin-3-glucoside equivalent per 100 gram of dry matter and calculated using the following equation:

$$\text{Anthocyanin content (mg / 100 g DW)} = \frac{[(A_{520\text{nm}} - A_{700\text{nm}})_{\text{pH}1.0} - (A_{520\text{nm}} - A_{700\text{nm}})_{\text{pH}4.5}] \times \text{MW} \times \text{D.F.}^* \text{T.E.V}}{(\epsilon \times W)}$$

where MW is the molecular weight of cyanidin-3-glucoside (449.2 g mol⁻¹), DF is the dilution factor (e.g., DF is 5 for an extract of

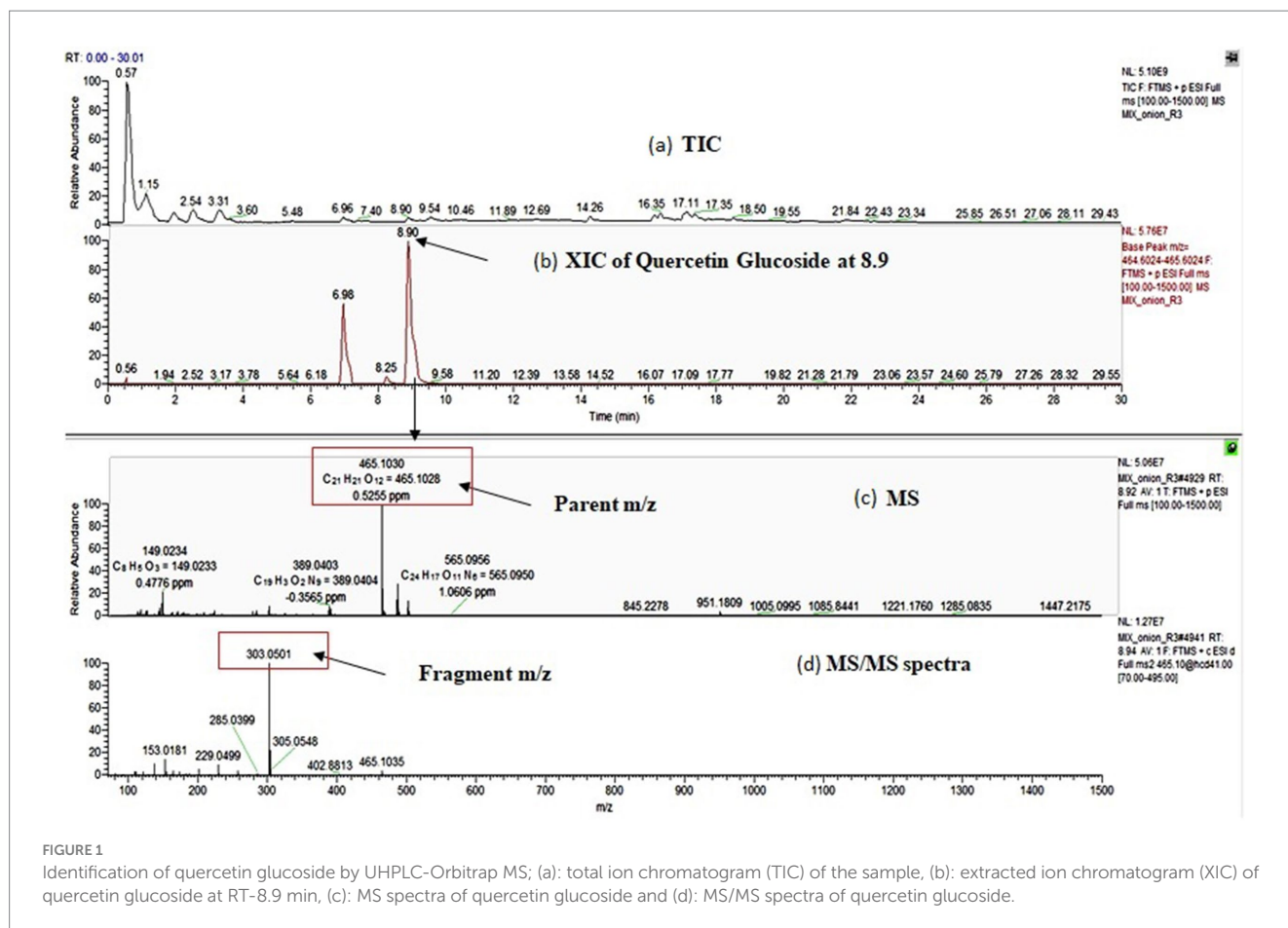


FIGURE 1

Identification of quercetin glucoside by UHPLC-Orbitrap MS; (a): total ion chromatogram (TIC) of the sample, (b): extracted ion chromatogram (XIC) of quercetin glucoside at RT-8.9 min, (c): MS spectra of quercetin glucoside and (d): MS/MS spectra of quercetin glucoside.

200 μL diluted to a final volume of 1,000 μL , ϵ is the molar extinction coefficient of cynidin-3-glucoside (26,900 $\text{LM}^{-1} \text{cm}^{-1}$), T.E.V is the total extract volume, and W is the weight of sample (Lee et al., 2008).

2.4 Determination of total phenol content (TPC)

The total phenol content was estimated using Folin–Ciocalteu reagent followed by Singleton and Rossi (1965) with some modifications suggested by Ateeq et al. (2023). Sample extraction (100 μL) was added to 200 μL of 10% (v/v) F-C reagent and thoroughly vortexed. To the vortexed mixture, 800 μL of 700 mM Na_2CO_3 was added and incubated for 2 h at room temperature. The reaction mixture (200 μL) was transferred in 96-well microplate, and the absorbance was taken at 765 nm against 95% methanol as blank on a SpectroStar Nano plate (BMG Labtech). Gallic acid was used as standard (100–1,000 $\mu\text{g}/\text{mL}$) for the preparation of calibration curve ($R^2 = 0.9996$), and the total phenol content was expressed as gallic acid equivalent (GAE) per 100 gram of onion peel.

2.5 Determination of total antioxidant activity (TAA)

Free radical scavenging assay was followed to assay the antioxidant activity of onion peel extract. The same extract was used for FRAP, DPPH, and ABTS assay.

2.5.1 Ferric reducing antioxidant power (FRAP) assay

Direct measurement of total antioxidant activity was estimated through FRAP assay which measures blue to purple color formed due to reduction of ferric tripyridyltriazine (Fe^{III} -TPTZ) complex (Benzie and Strain, 1999) with some modifications suggested by Sagar et al. (2020). FRAP working reagent was prepared by mixing 300 mM acetate buffer, pH 3.6, 10 mM TPTZ in 40 mM HCl and 20 mM $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in a ratio of 10:1:1 (v/v/v). It was prepared freshly as per requirement. Reaction mixtures containing 3.0 mL of working FRAP reagent and 100 μL test sample or standard solution of Trolox were mixed, vortexed, and incubated for 6 min at room temperature. Absorbance at 593 nm was taken using SpectroStar Nano plate (BMG Labtech) against a reagent black and corrected by methanol as blank. Synthetic analog of Tocopherol (Trolox) was taken as standard, and the total antioxidant activity was expressed as $\mu\text{mol}/\text{g}$ dry weight.

2.5.2 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay

Antioxidant activity was determined using DPPH radical as per the methodology described by Stoica et al. (2022) with some modifications. DPPH solution (0.1 mM) was made with ethanol, and 3.9 mL of it was added to 100 μL of onion peel extract or standard and incubated for 30 min at room temperature before reading the absorbance at 593 nm against ethanol as a blank on a SpectroStar Nano plate (BMG Labtech). DPPH solution without antioxidant was kept as control. Trolox equivalent antioxidant capacity (TEAC) was calculated using Trolox at 100–1000 μM as reference standard and

presented as $\mu\text{mol Trolox equivalent (TE)}/\text{g sample}$. Each sample/standard was read in triplicate.

2.5.3 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) assay

ABTS radical scavenging assay was estimated as per the method described by Re et al. (1999) and Sagar et al. (2020). ABTS radical was prepared by mixing 7 mM aqueous solution of ABTS diammonium salt with 2.45 mM potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) in a ratio of 1:1 (v/v) and incubated for 16 h in dark at room temperature. Fresh working solution was prepared by appropriate dilution of ABTS radical solution with ethanol till an absorbance of 0.700 ± 0.002 unit at 765 nm. A reaction mixture of 100 μL sample or standards and 3,900 μL of ABTS working solution were incubated for 6 min at room temperature before recording the spectrophotometric absorbance at 765 nm against 75% ethanol as blank. Trolox was used as reference standard at 100–1200 μM , and Trolox equivalent antioxidant capacity (TEAC) was expressed as $\mu\text{mol TE}/\text{g DW}$.

2.6 Statistical analysis

The results of TAC, TPC, FRAP, DPPH, and ABTS assay were presented as mean \pm standard deviation of three replicates (biological replications). Significance of difference between samples was evaluated through analysis of variance (ANOVA) using SAS base 9.2 (Tukey's test, $p < 0.05$). Multivariate analysis, that is, principal component analysis (PCA), cluster analysis, and correlation coefficients were carried out with JMP 9.0.0. Biplot between PCA 1 and PCA 2 was drawn using MS excel. Chemical structure was drawn on ChemDraw 19.1.

3 Results and discussion

3.1 LC–MS [UHPLC–Orbitrap MS] analysis

OPE of eight onion varieties was taken for high-resolution UHPLC–Orbitrap Mass Spectrometric analysis, and compound identification was performed against an in-house updated high-resolution accurate mass (HRAM) database, which was originally received from Thermo Fisher Scientific. The automated analyte identification and confirmation were based on the HRAM measurement of the precursor and its characteristic productions, each within ± 5 ppm of mass error and retention time tolerance of ± 0.1 min. Matching of the isotopic pattern (by $>90\%$) was considered as an additional filter. For example, quercetin glucoside was identified based on the precursor ion ($m/z = 465.1030$) with a mass error of 0.5 ppm (as observed in MS spectra) (Figure 1). It was above the threshold intensity of 5,000. In addition, the detection of characteristic fragment ($m/z = 303.0501$) supported its identification (as observed in MS/MS spectra). We identified 49 polyphenolic compounds including 33 anthocyanin (Table 2, compounds 14–46), 8 flavanol (6–13), 4 flavones (1–4), and 1 each of pyranoanthocyanin (47), chalcone (5), phenolic acid (48), and ellagitannins (49). Recoveries of reference standard quercetin and pelargonidin-3-O-glucoside were used for relative quantification of identified

compounds. Since reference standards of all compounds were not available, pelargonidin-3-O-glucoside was used for quantitation of all anthocyanin, and quercetin was used for quantitation of all flavonoids.

3.1.1 Flavanol

Flavanols are versatile class of flavonoid and characterized to have significant role in auxin transport and nodule development in legumes and provide protective interface against abiotic and biotic stress (Petrucci et al., 2013). Nutritionally, it has potential health benefits against cardiovascular disease, mutagenesis owing to its antioxidant properties (D'Andrea, 2015). As presented in Table 2, eight peaks were putatively identified as flavanol which include two isorhamnetin glycosides (Table 2, compounds 7–8), two quercetin glycosides (12–13), one quercetin dimer (11), one myricetin (10), one kaempferol glycosides (9), and one dihydromyricetin or amplexin (6). Quercetin glucoside appeared on two retention time (t_R) 8.9 and 8.96 with baseline separation having same precursor ion $m/z = 465.1$ and fragment ion $m/z = 303.05$ which indicates that both compounds may exist in isomeric forms (Figure 1). Anthology suggests that quercetin exists in four mono-glycoside forms with a substitution at positions 4' (quercetin 4'-glucoside) and 3' (quercetin 3'-glucoside) in aromatic ring B and positions 3 (quercetin 3-glucoside) and 7 (quercetin 7-glucoside) of γ -benzopyrone ring (Kwak et al., 2017; Lee et al., 2012). Another flavonoid isorhamnetin glucoside also eluted at different (t_R) 10.70 and 10.77 min. Having same elemental composition $\text{C}_{22}\text{H}_{22}\text{O}_{12}$ with a molecular (M^+) ion $m/z = 479.12$ and a characteristic fragment ion peak $m/z = 317.07$ suggest the isomeric presence of compound. Literature reports two forms of isorhamnetin glucoside having glucosyl substitution at 4' Carbon (isorhamnetin 4'-glucoside) and at 3 position in flavanol skeleton (isorhamnetin 3-glucoside) (Bonaccorsi et al., 2005; Park and Lee, 1996). Kaempferol rhamnose malic acid was identified based on peak for molecular ion $m/z = 549.12$ and characteristic fragment ion $m/z = 313.07$. Myricetin and dihydromyricetin (amplexin) were also identified in onion peel extract. Taxifolin and their conjugated glycosides are reported in onion bulbs (Fossen et al., 1998), while there is limited information about the presence of dihydromyricetin in onion. Yang et al. (2020) reported dihydromyricetin 3-O-rhamnoside along with dihydroquercetin 3-O-rhamnoside in onion. Kaempferol was the only acylated flavanol identified. Quercetin, isorhamnetin, myricetin, kaempferol, and its conjugated glycosides are most abundant flavonols in onion (Rodríguez Galdón et al., 2008; Slimestad et al., 2007).

3.1.2 Anthocyanin

Similar to flavanol, 34 anthocyanin compounds (Table 2, compounds 14–46) were putatively identified based on molecular and product ion peak with less than 5 ppm mass error. For instance, delphinidin-3, 5-diglucoside (25) was eluted at 6.98 min and identified based on the characteristic fragment $m/z = 303.05$ (Figure 2). Cyanidin-3-(6-malonylglucoside) with elemental composition $\text{C}_{24}\text{H}_{23}\text{O}_{14}$ ($t_R = 8.49$ min) was identified based on observed parent molecular ion peak $m/z = 535.11$, and its identity was further confirmed by characteristic product ion $m/z = 287.1$ for cyanidin aglycone. In similar way, 34 anthocyanins which include 10 cyanidin (14–23), 10 delphinidin (24–33), 4 peonidin (39–42), 4 petunidin (43–46), 3 pelargonidin (36–38), and 2 malvidin (34–35) were

TABLE 2 LC-MS [UHPLC-Orbitrap MS] characterization profile of putative phenolic compounds identified in OPE of eight differentially pigmented onion varieties.

S. No	Compound name	Formula	m/z Apex	RT measured	Fragment	Measured area (value × 10,000,000)								Minimum	Maximum
						Dark red		Red			Light red	White			
						BDR	BRJ	BSR	BRD	BSK	BKN	BSW	BSU		
Flavones															
1	Apigenin glucoside I	C ₂₁ H ₂₀ O ₁₀	433.11	9.92	271.06									0	2.01
2	Chrysoeriol	C ₁₆ H ₁₂ O ₆	301.07	12.83	286.05									2	3.28
3	Isovitexin	C ₂₁ H ₂₀ O ₁₀	433.11	9.49	415.1, 313.07									0.81	2.43
4	Luteolin	C ₁₅ H ₁₀ O ₆	287.05	12.52	287.05									17.61	59.77
Chalcones															
5	Butein	C ₁₅ H ₁₂ O ₅	273.08	11.25	137.02									0	0.36
Flavonols															
6	Ampeloptin	C ₁₅ H ₁₂ O ₈	321.06	7.96	153.02									1.2	1.43
7	Isorhamnetin hexoside I	C ₂₂ H ₂₂ O ₁₂	479.12	10.7	317.07									0	1.28
8	Isorhamnetin hexoside II	C ₂₂ H ₂₂ O ₁₂	479.12	10.77	317.07									0.69	211.43
9	Kaempferol rhamnose malic acid	C ₂₅ H ₂₄ O ₁₄	549.12	9.15	313.07									9.81	117.97
10	Myricetin	C ₁₅ H ₁₀ O ₈	319.04	5.35	133.03									0.29	98.78
11	Quercetin dimer	C ₃₀ H ₂₀ O ₁₄	605.09	12.2	301.03									2.31	15.56
12	Quercetin glucoside I	C ₂₁ H ₂₀ O ₁₂	465.10	8.9	303.05									18.97	1365.34
13	Quercetin glucoside II	C ₂₁ H ₂₀ O ₁₂	465.10	6.98	303.05									10.48	1365.34
Anthocyanin															
14	Cyanidin	C ₁₅ H ₁₁ O ₆	287.05	12.51	287.05									1.25	325.47
15	Cyanidin-3-(6-malonylglucoside)	C ₂₄ H ₂₃ O ₁₄	535.11	8.49	535.11, 287.1									0.64	1203.81
16	Cyanidin-3-(6-succinylglucoside)	C ₂₅ H ₂₅ O ₁₄	549.12	9.13	549.12									9.52	117.97
17	Cyanidin-3-5-diglucoside (cyanin)	C ₂₇ H ₃₁ O ₁₆	611.16	7.34	611.16, 287.1									4.97	82.65
18	Cyanidin-3-acetylglucoside	C ₂₃ H ₂₃ O ₁₂	491.12	8.31	491.12, 287.1									2.76	42.5

(Continued)

TABLE 2 (Continued)

S. No	Compound name	Formula	m/z Apex	RT measured	Fragment	Measured area (value × 10,000,000)								Minimum	Maximum
						Dark red		Red			Light red	White			
						BDR	BRJ	BSR	BRD	BSK	BKN	BSW	BSU		
19	Cyanidin-3-galactoside (ideain)	C ₂₁ H ₂₁ O ₁₁	449.11	7.37	449.11, 287.1									0.53	190.52
20	Cyanidin-3-O-glucoside	C ₂₁ H ₂₁ O ₁₁	449.11	7.37	449.11, 287.1									0.53	190.52
21	Cyanidin-3-O-rhamnoside	C ₂₁ H ₂₁ O ₁₀	433.11	9.51	433.11									0.85	2.44
22	Cyanidin-3-sophoroside	C ₂₇ H ₃₁ O ₁₆	611.16	7.34	611.16, 287.1									4.97	82.65
23	Cyanidin-3-O-(200galloyl)-galactoside	C ₂₈ H ₂₄ O ₁₅	601.12	12.34	285.04									0	1.25
24	Delphinidin-3-(6-malonylglucoside)	C ₂₄ H ₂₃ O ₁₅	551.1	11.17	303.05, 127									5.51	26.31
25	Delphinidin-3-5-diglucoside	C ₂₇ H ₃₁ O ₁₇	627.16	6.98	303.05, 127, 97.03, 85.03									2.43	124.61
26	Delphinidin-3-galactoside	C ₂₁ H ₂₁ O ₁₂	465.1	10.18	465.1, 303.1, 127.04									10.48	1365.34
27	Delphinidin-3-O-arabinoside	C ₂₀ H ₁₉ O ₁₁	435.09	10.17	435.09, 303.1, 127.04									1.24	1.64
28	Delphinidin-3-O-(6-O-feruloyl) monoglucoside	C ₃₁ H ₂₉ O ₁₅	641.15	12.43	303.05, 97.03, 85.03									0.91	1.45
29	Delphinidin-3-O-glucoside-pyruvic acid	C ₂₄ H ₂₁ O ₁₄	533.09	8.46	127.04, 97.03, 85.03									2.39	3.82
30	Delphinidin-3-O-rutinoside (Tulipanin)	C ₂₇ H ₃₁ O ₁₆	611.16	7.34	611.16, 85.03									4.97	82.65
31	Delphinidin-3-sophoroside-5-glucoside	C ₃₃ H ₄₁ O ₂₂	789.21	4.82	303.05, 127									1.42	3.89
32	Delphinidin-3-xyloside	C ₂₀ H ₁₉ O ₁₁	435.09	10.17	435.09, 303.1, 127.04									1.24	1.64
33	Delphinidin	C ₁₅ H ₁₁ O ₇	303.05	11.41	303.05, 127									14.78	2850.25
34	Malvidin-3-arabinoside	C ₂₂ H ₂₃ O ₁₁	463.12	7.59	463.12									11.67	41.57
35	Malvidin-pyruvate	C ₂₀ H ₁₅ O ₉	399.07	2.11	399.07									0	0.77
36	Pelargonidin-3-glucoside (Callistephin)	C ₂₁ H ₂₁ O ₁₀	433.11	9.48	433.11, 271.1									0.81	2.43

(Continued)

TABLE 2 (Continued)

S. No	Compound name	Formula	m/z Apex	RT measured	Fragment	Measured area (value × 10,000,000)								Minimum	Maximum
						Dark red		Red			Light red	White			
						BDR	BRJ	BSR	BRD	BSK	BKN	BSW	BSU		
37	Pelargonidin-3-malonylglucoside	C ₂₄ H ₂₃ O ₁₃	519.11	9.02	519.11, 271.1									1.66	2.49
38	Pelargonidin	C ₁₅ H ₁₁ O ₅	271.06	13.1	271.06									2.17	5.41
39	Peonidin-3-glucoside	C ₂₂ H ₂₃ O ₁₁	463.12	7.65	463.12, 301.1									5.33	41.57
40	Peonidin-3-O-arabinoside	C ₂₁ H ₂₁ O ₁₀	433.11	9.5	433.11									0.85	2.44
41	Peonidin-3-O-xyloside	C ₂₁ H ₂₁ O ₁₀	433.11	9.5	433.11									0.85	2.44
42	Peonidin	C ₁₆ H ₁₃ O ₆	301.07	11.21	301.07									0.39	14.22
43	Petunidin 3-5-diglucoside	C ₂₈ H ₃₃ O ₁₇	641.17	8.96	317.07									11.76	30.33
44	Petunidin 3-arabinoside	C ₂₁ H ₂₁ O ₁₀	433.11	9.6	433.11									1.51	2.39
45	Petunidin 3-glucoside	C ₂₂ H ₂₃ O ₁₂	479.12	10.77	317.07									0.69	211.43
46	Petunidin	C ₁₆ H ₁₃ O ₇	317.07	12.81	317.07									1.09	452.16
Pyranoanthocyanin															
47	Vitisin A-delphinidin-glucoside	C ₂₄ H ₂₁ O ₁₄	533.09	8.46	127.04, 97.03, 85.03									2.39	3.82
Phenolic Acid															
48	Protocatechuic acid hexoside	C ₁₃ H ₁₆ O ₉	317.09	1.66	137.02									0	0.98
Tannins															
49	Trigalloyl levoglucosan IX	C ₂₀ H ₂₆ O ₂₂	619.1	14.49	153.02									2.65	7.87



Each compound with chemical formula, mass/charge ratio, and major frequent ion with intensity > 5,000 was presented. Relative abundance in varieties (dark red var. BDR and BRJ; Red var. BSR, BRD, and BSK; light red var. BKN and white var. BSU and BSN) based on absolute area measured was presented as heat map.

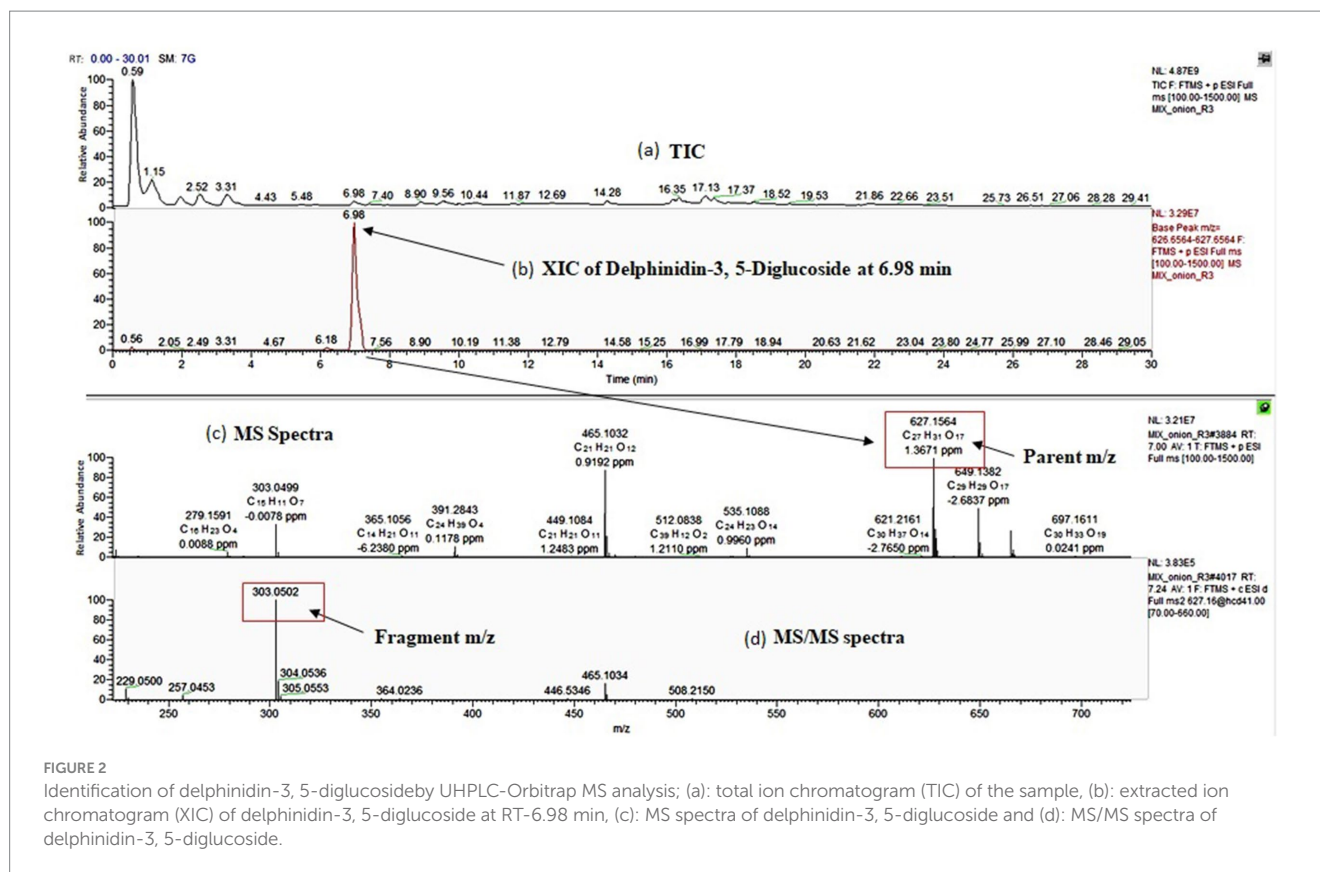


FIGURE 2

Identification of delphinidin-3, 5-diglucoside by UHPLC-Orbitrap MS analysis; (a): total ion chromatogram (TIC) of the sample, (b): extracted ion chromatogram (XIC) of delphinidin-3, 5-diglucoside at RT-6.98 min, (c): MS spectra of delphinidin-3, 5-diglucoside and (d): MS/MS spectra of delphinidin-3, 5-diglucoside.

identified in this study. Among all anthocyanins, six were acylated glycosides, five were aglycone, and three were doubly substituted (Table 2). We observed maximum of 30–33 anthocyanin glycosides in dark red and red onion varieties and minimum of 9–11 anthocyanin in white onion (BSU and BSW). Downes et al. (2009) reported ten anthocyanin glycosides of cyanidin and peonidin but did not found petunidin, pelargonidin, and malvidin. However, there is limited information regarding the presence of malvidin in onion. Petersson et al. (2008) reported malvidin-3-glucoside in red onion bulb (Petersson et al., 2008) and later by Yang et al. (2020). Vitisin A-delphinidin glucoside (47) is a pyranoanthocyanin conjugated with delphinidin glucoside which was also identified in onion peel extract. The presence of anthocyanin oligomers or pyranoanthocyanin has been reported in grapes, rose, and red onion (Fossen and Andersen, 2003; Santos-Buelga et al., 2014; Rentzsch et al., 2007).

3.1.3 Flavones and other compounds

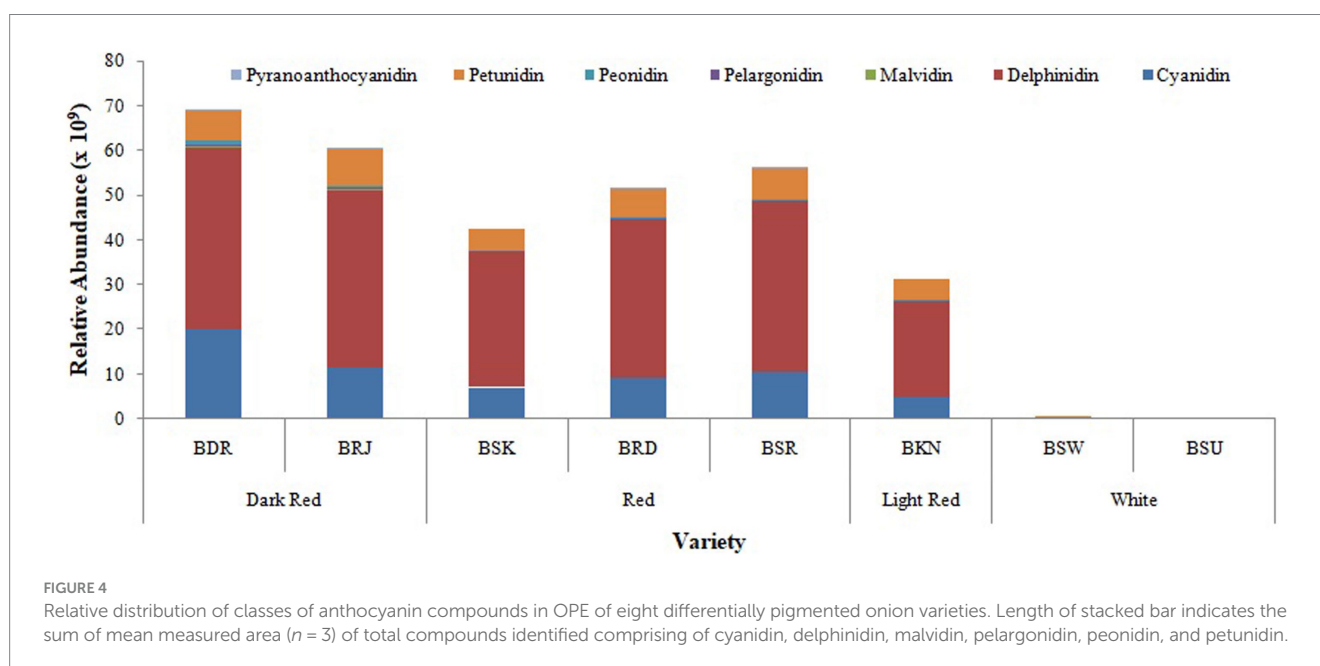
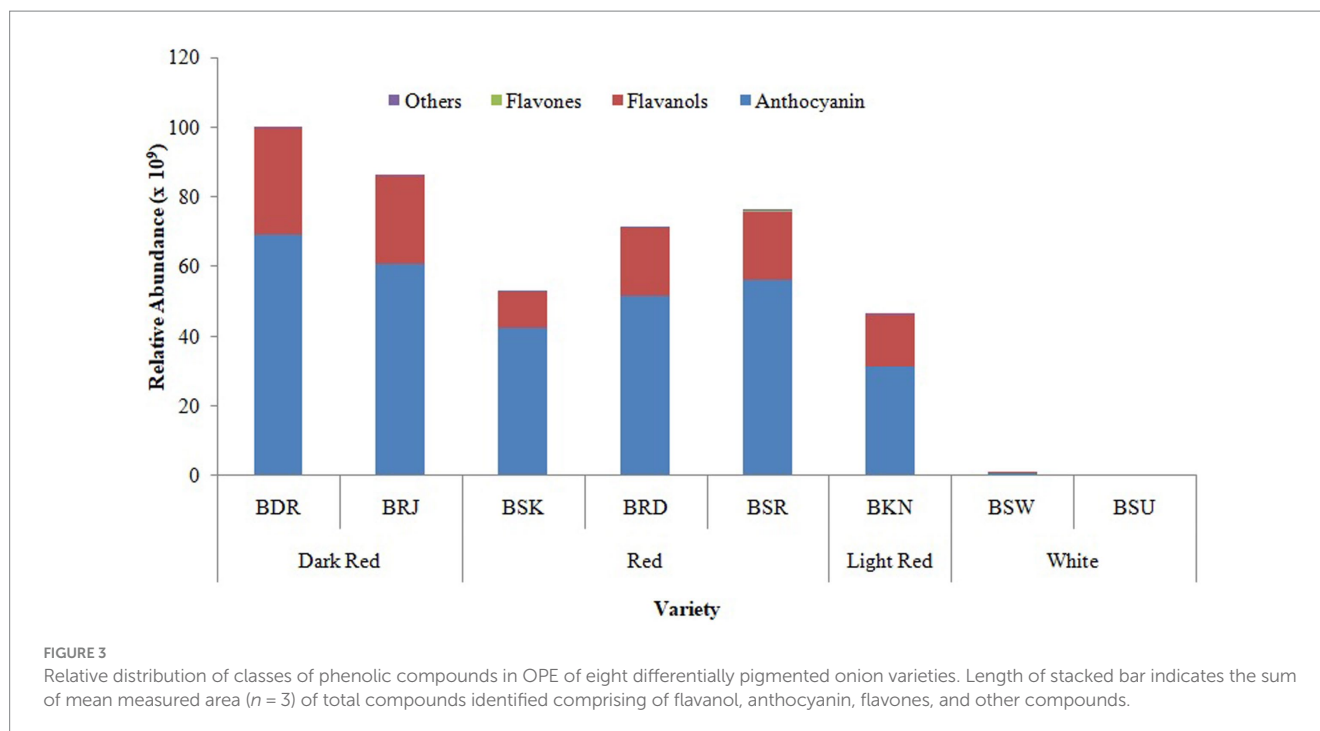
Flavones (3-deoxyflavanol) are a class of flavonoids widely present in fruits and vegetables. Five flavones (1–4), apigenin, luteolin, chrysoeriol, and isovitexin were putatively identified from onion peel extract with low abundance. Low abundance of flavones in onion has been hypothesized (Kothari et al., 2020), but very few reports are available. Yang et al. (2020) reported apigenin 6-C-glucoside and luteolin 7-O-glucuronid in onion bulb. A degradation product of anthocyanin, protocatechuic acid hexoside, was also identified based on precursor ion peak $m/z = 317.09$ and characteristic fragment ion peak $m/z = 137.02$ (Ly et al., 2005). 2',3,4,4'-tetrahydroxychalcone was also observed having a molecular ion (M^+) $m/z = 273.08$ and characteristic fragment ion peak $m/z = 137.02$. Chalcones are

abundant in bright yellow color onion (Schwinn et al., 2016). A hydrolysable tannin, trigalloyl levoglucosan, with a precursor $m/z = 619.1$ and fragment ion 153.02 was also identified in this study. It is levoglucosan acylated with gallic acid (3, 4, 5-Trihydroxybenzoic acid).

3.2 Relative distribution of polyphenolic compounds

The relative distribution of major classes of putatively identified polyphenolic compounds in differentially pigmented onion varieties is presented in Figure 3. Based on the absolute area response of the identified peak, it was noted that out of 49 identified phenolic compounds, maximum of 43 were detected in *var. BSR* which include nine flavanol, four flavones, and thirty anthocyanin glycosides. In white onion varieties BSU, only nine compounds were identified including five flavanol and eleven anthocyanin.

Flavanols are hydrophilic compound with β -glycosidic linkages which makes it a most bioavailable antioxidant in human diet (Price and Rhodes, 1997). Onion bulbs are reported to have higher flavanol content than anthocyanin (Metrani et al., 2020; Khandagale and Gawande, 2019) and are reportedly only 10% of the total polyphenols (Rodrigues et al., 2017) in bulb. In onion peel extract (OPE) of differentially pigmented onion varieties, anthocyanin was the most abundant polyphenolic compounds than flavanol. Albishi et al. (2013) also reported higher flavonoid content in red onion skin than bulb. Inner scales of onion bulbs have lower flavonoid level than outer scales (Patil and Pike, 1995). Among flavanol, quercetin glucoside was most



abundant flavanol observed across pigmented onion varieties followed by isorhamnetin, kaempferol, and myricetin. Glucose is the exclusive moieties in quercetin attached to 3, 7, or 4' position of aglycone. Quercetin 4'-glucoside and quercetin 3,4'-glucosides are widely reported to be the most abundant flavanol in onion bulbs (Pucciarini et al., 2019). The abundance of all the flavanol was very low in white onion cultivars in comparison with others. Price and Rhodes (1997) also reported quercetin and its glycosides as most predominant flavanol, and it was higher in red onion varieties Red baron, Rose, and Rijnsburger than white variety albino (Price and Rhodes, 1997).

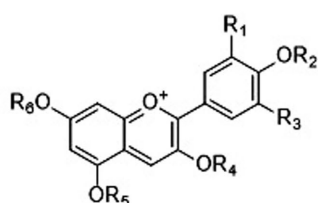
Flavones are 2-phenyl-1-benzopyran-4-one, having additional double bond between C2 and C3 of flavonoid skeleton and no hydroxyl group at C3 position. It is reported to have lower antioxidant potential

and poor absorption in human intestine but has significant role in biotic defense against insect and microbes (Hostetler et al., 2017). In OPE of differentially pigmented varieties, flavone was most abundant in light red varieties (BSR), less abundant in red varieties, and absent in white onions. A chalcone, butein, was observed only in *var.* BRD and protocatechuic acid in *var.* BSK. Trigalloyl levoglucosan was observed in all red varieties but found absent in white varieties (Table 2).

Among anthocyanin, delphinidin was the most predominant class of anthocyanin followed by cyanidin > petunidin > peonidin > malvidin > pelargonidin in most of the cultivars (Figure 4). As presented in Table 3, relative abundance of cyanidin and its glycosides observed maximum in dark red *var.* BDR and BRJ and gradually lower level in red *var.* BSR, BRD, BSK, and light red *var.* BKN, while it was minimum in

TABLE 3 Percentage of class of anthocyanin present in OPE of different varieties.

Classes of anthocyanin compound	Class of anthocyanin in OPE (%)							
	Dark Red			Red		Light Red	White	
	BDR	BRJ	BSR	BRD	BSK	BKN	BSW	BSH
Cyanidin	30	20	19	18	17	16	7	6
Delphinidin	60	68	70	71	73	72	88	87
Petunidin	8	11	11	11	10	12	5	6
Others	2	1	0	0	0	0	0	1



	R1	R2	R3	R4	R5	R6
14	H	H	OH	H	H	H
15	H	H	OH	6"-malglc	H	H
16	H	H	OH	6"-salglc	H	H
17	H	H	OH	glc	glc	H
18	H	H	OH	3"-acglc	H	H
19	H	H	OH	gal	H	H
20	H	H	OH	glc	H	H
21	H	H	OH	rham	H	H
22	H	H	OH	soph	H	H
24	OH	H	H	6"-malglc	H	H
25	OH	H	H	glc	glc	H
26	OH	H	H	gal	H	H
27	OH	H	H	ara	H	H
28	OH	H	H	6"-ferglc	H	H
29	OH	H	H	3"-pyrglc	H	H
30	OH	H	H	rut	H	H
31	OH	H	H	soph	glc	H
32	OH	H	H	xyl	H	H
33	OH	H	H	H	H	H
34	OCH ₃	H	OCH ₃	ara	H	H
35	OCH ₃	H	OCH ₃	H	H	H
36	H	H	H	glc	H	H
37	H	H	H	malglc	H	H
38	H	H	H	H	H	H
39	H	H	OCH ₃	glc	H	H
40	H	H	OCH ₃	ara	H	H
41	H	H	OCH ₃	xyl	H	H
42	H	H	OCH ₃	H	H	H
43	OH	H	OCH ₃	glc	GLC	H
44	OH	H	OCH ₃	ara	H	H
45	OH	H	OCH ₃	Glc	H	H
46	OH	H	OCH ₃	H	H	H

FIGURE 5

Class of putative anthocyanin compounds identified from the OPE of eight differentially pigmented onion varieties and its substitution pattern. Cyanidin (14–22); delphinidin (24–33); malvidin (34–35); pelargonidin (36–38); peonidin (39–42); petunidin (43–46). Compound numbering is as per Table 2. Abbreviation are as follows: *mal*-malonyl, *sal*-succinyl, *fer*-feruloyl, *pyr*-pyruvic acid, *ac*-acetyl, *glc*-glucose, *gal*-galactose, *ara*-arabinose, *rham*-rhamnose, *soph*-sophorose, *xyl*-xylose, *rut*-rutinose.

white var. BSU. Contrary of cyanidin, percentage abundance of delphinidin and its glycoside was observed minimum in dark red varieties, slightly higher in red and light red var. and maximum in white onions. Relative abundance of cyanidin and delphinidin might be the key factor associated with differential pigmentation of onion bulb. Cyanidin glycosides were observed with most acylation followed by pelargonidin. Acylation is predominant in dark red and red onion cultivars than light red and white. Cyanidin-3-(6-malonylglucoside), delphinidin, and delphinidin-3-galactoside were the predominant pigment in dark red var. BDR and BRJ, and its abundance suggests a key role in differential pigmentation pattern. Downes et al. (2009) also reported predominant presence of cyanidin-3-(6-malonylglucoside) in dark red onion. Similar reports were made by Fossen et al. (1996) and Donner et al. (1997). Most abundant aglycone across all the varieties was delphinidin followed by petunidin and aglycone form of both are more abundant in colored cultivars than white. In cyanidin glycoside, aglycone form is more abundant in white than colored varieties. As presented in Figure 5, third carbon position in benzopyrylium ring was the most preferred substitution followed by fifth carbon position. Glucose (glc), galactose (gal), rhamnose (rham), sophorose (soph), xylose (xyl), arabinose (ara), and rutinose (rut) were the observed glycoside substitution, and among these, glucoside and galactoside were the most preferred.

3.3 Principal component analysis (PCA) and cluster analysis

PCA was performed on the relative abundance data obtained for the putatively assigned anthocyanin compounds (14–47). Principal component score of eight varieties varying on PC1 (66.72%) and PC2 (14.75%) is presented in Figure 6. Eight distinctly pigmented varieties under investigation grouped in four groups. White varieties BSU and BSW grouped together having negative correlation with both PC1 and PC2. Varieties BSK, BRD, and BKN grouped together and showed very low variation with PC1 and considerable variation on PC2. Red var. BSR and dark red var. BRJ showed very positive correlation with PC1 and PC2. Dark red variety BRD showed very high positive correlation with PC1 and negative correlation with PC2. Examination of component pattern distribution (Supplementary Figure 1) on principle component axis revealed that substituted and acylated anthocyanin are strongly correlated with PC1 and show very less variation, whereas it is well distributed along PC2. Cyanidin (14–23) exhibited exclusive distribution on negative axis of PC2 and positive axis of PC1, whereas pelargonidin (36–38) on positive axis of PC1 and PC2. Among the five most abundant anthocyanin cyanidine-3-(6-malonylglucoside), delphinidin-3galactoside, delphinidin, petunidin 3-glucoside, and petunidin, all are

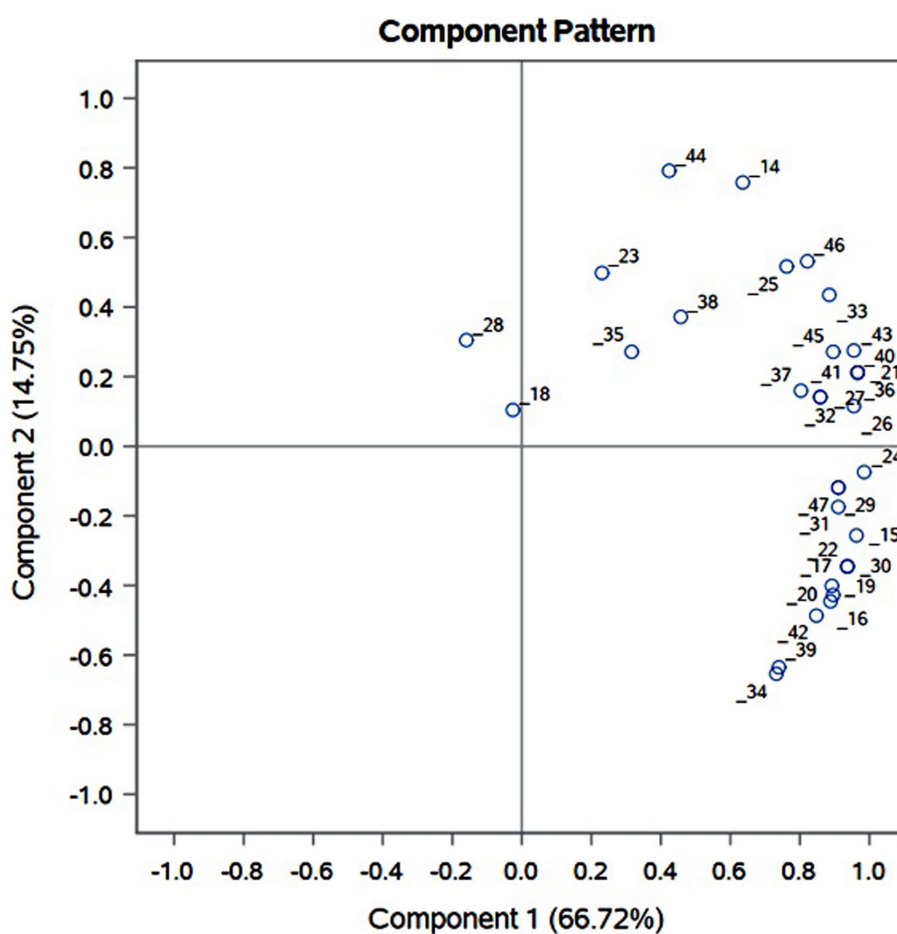


FIGURE 6

Principal component analysis (PCA) of anthocyanin compounds identified from OPE of differentially pigmented onion varieties, viz., Dark red var. BDR and BRJ; Red var. BSR, BRD, and BSK; Light red var. BKN; white var. BSU and BSW.

positively correlated with PC2 except cyanidine-3-(6-malonylglucoside). This suggests that preceding four anthocyanin compounds might be the key determinant of red color var. BSR, BRJ, and BRD while cyanidine-3-(6-malonylglucoside) in dark red var. BDR.

Varieties were well classified by cluster analysis supporting the color distribution pattern (Figure 7). At partial R square value 0.1, we observed two cluster, one with light red var. BKN and red var. BSK while other having red var. BSR and BRD and dark red var. BRJ. Both clades separate with dark red var. BDR at R square value of 2.8. White onion var. BSU and BSW formed a separated clade at R square value >0.4. PCA and cluster analysis revealed that red var. BSK and light red var. BKN have similar anthocyanin distribution pattern. Similarly, dark red var. BRJ exhibited similar distribution of anthocyanin that of red onion var. BSR and BRD.

3.4 Total anthocyanin and total polyphenol contents

Anthocyanin is a subclass of flavonoid compounds imparting diverse color to onion bulbs and possess various nutraceutical properties. As presented in Table 4, the mean total anthocyanin content in dark red varieties was maximum followed by red, light

red, and white varieties. Within the dark red varieties, the anthocyanin content in BDR (28.23 mg/100 g DW) was significantly high than BRJ (5.29 mg/100 g DW) with $p \leq 0.0001$ level. Anthocyanin content was observed at par in red varieties BRD, BSK, and BSR and in light red var. BKN. In white varieties, very low level of anthocyanin was observed, and both were not significantly different. Anthocyanin content in dark red var. BDR is ~3–5 times higher than red onion var. and ~7–8 times higher than light red varieties. Zhang et al. (2016) reported range of 0.75 ± 0.40 mg/100 g FW anthocyanin content in white, 9.64 ± 0.30 mg/100 g FW in yellow, and 29.99 ± 1.19 mg/100 g FW in red onion. Albishi et al. (2013) also reported more anthocyanin content in onion peel extract (OPE) than bulb.

Total phenol content (TPC) in OPE ranged from 1738.21 to 1757.76 mg GAE/100 g DW in dark red onion, 1306.58 to 1646.73 mg GAE/100 g DW in red onion, and 78.77 to 85.5 mg GAE/100 g DW in white varieties. As presented in Table 4, TPC in all category of OPE extract was significantly different among each other with probability level at $p \leq 0.0001$ level. Among red onion, TPC was maximum in var. BSR followed by var. BSK and BRD. Although OPE of light red onion BKN exhibited lower anthocyanin content than red onion, TPC was 1441.13 mg GAE/100 g DW which is higher than red onion var. BRD. High level of polyphenols in onion skin with similar range

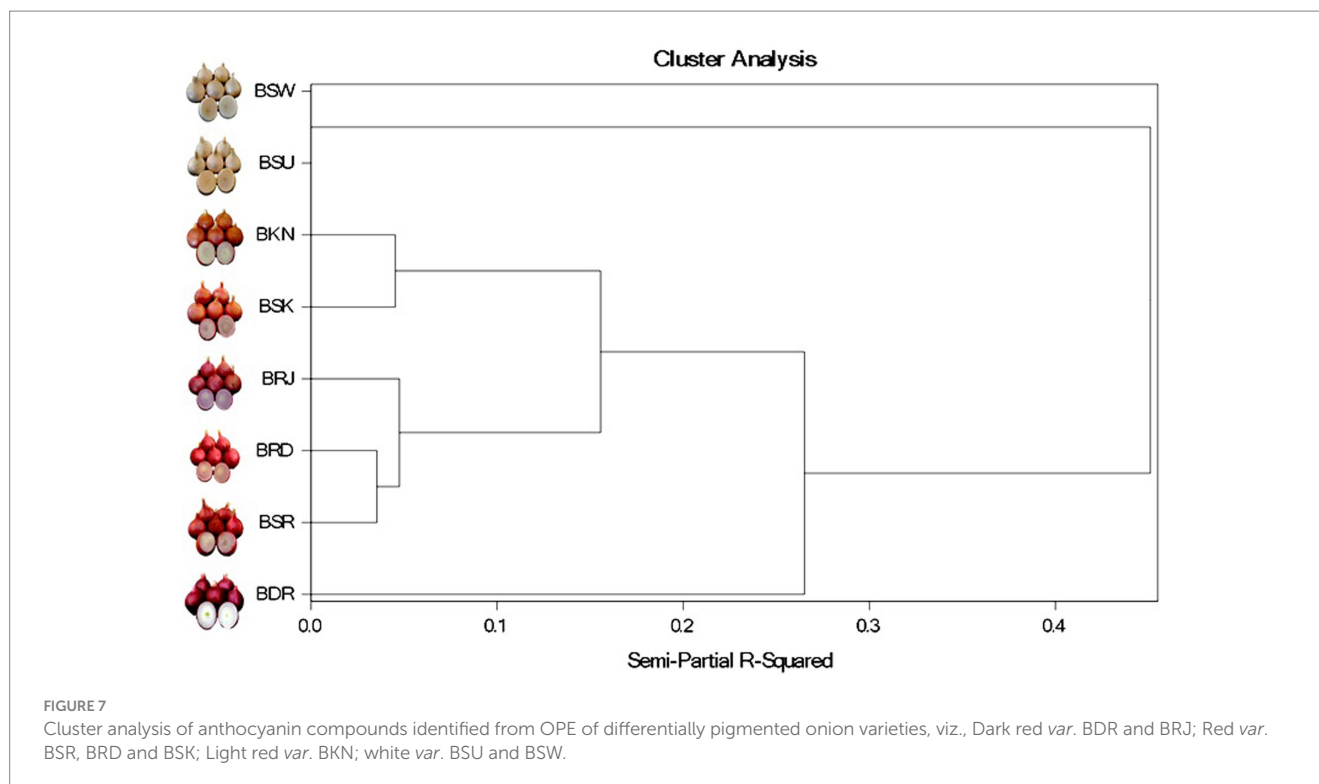


TABLE 4 Total phenol content (TPC), total anthocyanin content (TAC), and total antioxidant activity (TAA) in OPE of eight differentially pigmented onion varieties.

Color	Variety	Total anthocyanin content (mg/100gDW)	Total phenol content (mg/100gDW)	Antioxidant activity ($\mu\text{mol TE/gDW}$)		
				FRAP	ABTS	DPPH
Dark Red	Bhima Dark Red	28.23 ± 3.34^A	1738.21 ± 2.74^B	79.80 ± 0.93^A	286.70 ± 0.26^A	156.89 ± 7.67^A
	Bhima Raj	5.29 ± 0.28^{BC}	1757.76 ± 5.80^A	70.21 ± 2.18^B	215.12 ± 4.56^B	156.82 ± 2.90^A
Red	Bhima Super	3.03 ± 0.45^{CD}	1646.73 ± 1.71^C	66.60 ± 0.54^C	174.42 ± 2.36^C	147.49 ± 3.28^B
	Bhima Shakti	8.15 ± 0.25^B	1520.24 ± 10.45^D	64.99 ± 0.49^C	210.15 ± 4.57^B	136.54 ± 3.95^C
	Bhima Red	7.79 ± 0.88^B	1306.58 ± 2.41^E	50.92 ± 1.83^D	156.34 ± 2.60^D	111.22 ± 1.35^D
Light red	Bhima Kiran	4.51 ± 0.49^C	1441.13 ± 12.74^E	48.52 ± 0.48^E	119.47 ± 3.09^E	92.88 ± 4.96^E
White	Bhima Shweta	0.18 ± 0.05^D	85.50 ± 0.28^G	6.25 ± 0.03^F	42.00 ± 4.25^F	9.84 ± 1.10^F
	Bhima Shubra	0.11 ± 0.02^D	78.77 ± 0.25^G	4.71 ± 0.02^F	22.71 ± 2.66^G	8.72 ± 0.43^F
	<i>p</i> -value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
	CV (%)	17.36	0.55	2.02	2.19	3.77

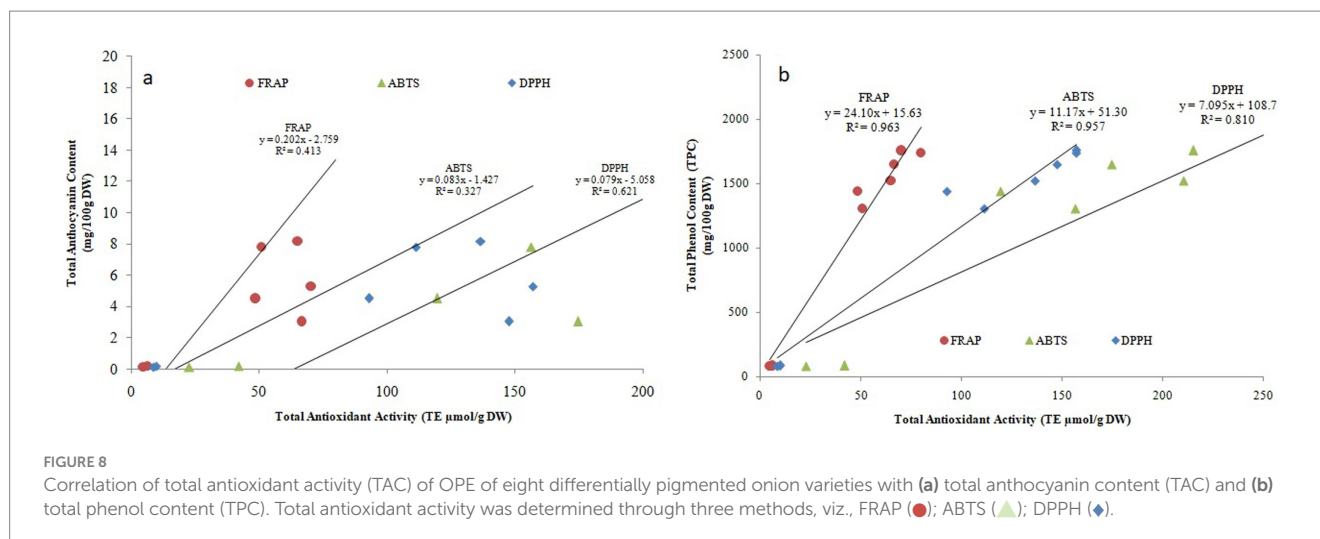
Data are presented as mean \pm SD of six parallel replication, and group letters were assigned based on Tukey's honest significant test (5%).

was reported in literature (Sagar and Pareek, 2020b; Lee et al., 2015; Sagar et al., 2020).

3.5 Total antioxidant activity

Antioxidant activity has been used widely to characterize various food matrix for the ability to scavenge or neutralize free radicals (Pyrzynska and Pękal, 2013). However, there is no single versatile method to determine antioxidant activity accurately. Here, we followed three methods, viz., FRAP, DPPH, and ABTS, to estimate total antioxidant activity (TAA). The results were compared with water-soluble tocopherol analog Trolox and expressed as micromole

per gram. In all the three methods (FRAP, ABTS, and DPPH), the mean antioxidant activity was more in dark red varieties followed by light red and white varieties. The antioxidant activity ranged from 4.71 to 79.80 $\mu\text{mol/g DW}$, 22.71 to 286.7 $\mu\text{mol/g DW}$, and 8.72 to 156.89 $\mu\text{mol/g DW}$ in FRAP, ABTS, and DPPH methods, respectively. Total antioxidant activity was maximum in dark red variety BDR and minimum in white variety BSU. Among dark red varieties, BDR showed significantly high antioxidant activity than BRJ in all the three methods (Table 4). In red varieties, the antioxidant activity by FRAP method showed the significantly high value in BSR and significantly low in BRD. BSR and BSK showed similar level of antioxidant activity. All the three red varieties (BSR, BSK, and BRD) were significantly different for ABTS and DPPH activities with



maximum in BSR (DPPH method) and BSK (ABTS method). In both the methods (ABTS and DPPH), minimum was found in BRD variety. Within the white varieties, no significant difference was observed in BSW and BSU for FRAP and DPPH. However, significantly high antioxidant value was observed in BSW (42 $\mu\text{mol/g DW}$) compared to BSU (22.71 $\mu\text{mol/g DW}$) in ABTS method owing to the better level of polyphenol content.

In all the methods, dark red varieties exhibited highest antioxidant activity, and white varieties had lowest which is evident from the corresponding anthocyanin and polyphenol content. To investigate the profound factor contributing to antioxidant activity of onion peel extract, we performed a correlation analysis among total phenols, total anthocyanin, and three antioxidant methods. As presented in Figure 8, the coefficient of correlation (R^2) of antioxidant activity was more in all three methods for TPC than anthocyanin content (TAC). The coefficient of correlation (R^2) for TAA and TPC ranged from 0.8105 to 0.9637, while it was considerably low with TAC (0.3271–0.6211). Lee et al. (2015) also observed poor correlation of total antioxidant capacity and anthocyanin content in white, yellow, and red onion. Zhang et al. (2016) reported high correlation between total polyphenols and antioxidant activity, but contrary to our finding, they also reported highly positive correlation between total anthocyanin content and total antioxidant content. In bulb of two red onion varieties, a strong correlation between total flavanol content and antioxidant activity was also observed but reported a poor correlation between total phenol and anthocyanin (Metrani et al., 2020).

4 Conclusion

Onion peels of red and dark red onions are very rich source of polyphenolic compounds having nutraceutical potential. Present study putatively identified 49 polyphenolic compounds from outer papery peel of eight distinctly pigmented onion varieties. Identified phenolic compounds comprised of 33 anthocyanin, 13 flavanol, 4 flavones, and 1 each of pyranoanthocyanin, chalcone, phenolic acid, and tannin. Anthocyanin was the most abundant compound followed by flavanol. Quercetin and its glycosides were the predominant flavanol, whereas cyanidin, delphinidin, and its glycosides were predominant anthocyanin. Acylated anthocyanin was predominant in dark red and red onion varieties. Cyanidin-3-(6-malonylglucoside),

delphinidin, and delphinidin-3-galactoside were the predominant pigment in dark red var. BDR and BRJ, and its abundance suggests a key role in differential pigmentation pattern. Antioxidant activity showed strong association with total polyphenol content, whereas very low association was observed with total anthocyanin content. PCA and cluster analysis grouped red var. BSK with light red var. BKN and dark red var. BRJ with red var. BSR and BRD. This research suggests that utilizing onion peel extracts could enhance the development of functional foods and dietary supplements, promoting sustainability and health benefits. Furthermore, there is a need for quantitative profiling of nutraceutically important polyphenolics from peels of widely processed onion varieties and to develop efficient extraction process as well as associated product for harnessing wealth potential of this emerging bio-waste.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary material, further inquiries can be directed to the corresponding authors.

Author contributions

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fsufs.2024.1469635/full#supplementary-material>

SUPPLEMENTARY FIGURE 1

Distribution of putatively identified anthocyanin compounds along the axis of principal component 1 (PC1) and principal component 2 (PC2) is shown in Supplementary File. Substituted and acylated anthocyanins are strongly correlated with PC1 and show very less variation, whereas it is well distributed along PC2.

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