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Research Article

Physicochemical properties, organic acid composition and free amino acid profiles in selected *Cornus mas* L. genotypes from the Çoruh Valley

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Abstract

Cornus mas L. (cornelian cherry) is a species widely used from traditional consumption to modern industrial applications due to its high nutritional content, richness in phenolic compounds, and functional food potential. This study aimed to comprehensively evaluate the physicochemical properties, organic acid composition, and free amino acid profiles of 15 cornelian cherry genotypes selected from the Çoruh Valley, one of Turkey's important biodiversity centers. Fruit samples were collected at full physiological maturity, and TSS, titratable acidity, pH, sugar composition, ascorbic acid, and tannin contents were analyzed using standard methods. Organic acids were determined by HPLC-UV, and free amino acids were determined by HPLC with OPA/FMOC derivatization. All measured traits differed significantly among genotypes ($p < 0.05$). Malic acid ranged from 38.12 to 251.34 mg/100 g, and total organic acids from 588.89 to 1038.15 mg/100 g. Free amino acid contents ranged from 71.34 to 93.14 mg/100 g, with the highest values in the G7 and G5 genotypes. This study demonstrates that the Çoruh Valley is an important hotspot of genetic diversity for cornelian cherry and contains genotype groups suitable for different uses. Overall, the findings provide a biochemical basis for selecting genotypes for breeding, nutritional applications, and industrial processing.

Keywords: amino acid profile; *Cornus mas*; genetic variation; HPLC; nutritional quality; organic acid

Introduction

Cornelian cherry is rich in vitamins, phenolic compounds, iridoids, organic acids, and amino acids, and has long been used in traditional medicine and the food industry (Pawlowska *et al*., 2010; Czerwińska and Melzig, 2018). The taste, aroma, and nutritional quality of cornelian cherry fruit are largely determined by

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organic acids, sugars, amino acids, and phenolic compounds (Demir and Kalyoncu, 2003; Tural and Koca, 2008; Rad et al., 2016).

Organic acids affect the sensory profile of the fruit and play a critical role in energy metabolism, cell homeostasis, and ripening processes. Various studies have reported that malic acid is the dominant organic acid in cornelian cherry fruits (Tural and Koca, 2008; Martinović and Cavoski, 2020). The amino acid profile determines the protein quality, flavor component formation, and metabolic activity of the fruit (Antoniewska-Krzeska *et al*., 2022). However, comprehensive amino acid profile studies based on multiple genotype comparisons for cornelian cherry are still limited in the literature (Matkarimova *et al*., 2023).

Turkey, especially the Black Sea and Eastern Anatolia regions, is considered one of the most important gene centers of cornelian cherry (Ercisli *et al*., 2011). The Çoruh Valley, located within the Caucasus Biodiversity Hotspot, exhibits high genetic diversity (Eken *et al*., 2016). The topographic diversity and microclimatic conditions in the region lead to wide variation in fruit composition. All genotypes sampled in this study originated from naturally growing wild populations rather than cultivated orchards, allowing a realistic assessment of natural genetic diversity.

The study was conducted during the 2024 harvest season, and fruits were collected at full physiological maturity based on external coloration, firmness, and minimum soluble solid content (TSS ≥ 15 °Brix), which is commonly used as a maturity index for cornelian cherry. Harvesting was performed during the optimal ripening window for the region (late August to mid-September), when biochemical composition reaches its highest stability.

Although many studies report general biochemical characteristics of *Cornus mas*, there remains a lack of genotype-based datasets that integrate physicochemical traits, organic acids, and amino acid profiles together, limiting both breeding efforts and quality-oriented selection strategies. Therefore, a more problem-oriented assessment of how genetic variation shapes key biochemical parameters is required. This study aimed to characterize the physicochemical traits, organic acid composition, and free amino acid profiles of 15 wild genotypes from the Çoruh Valley and to evaluate their biochemical diversity.

Materials and Methods

Plant material and sampling

Fruit samples were obtained from natural cornelian cherry populations located at an altitude of 733-1448 m in the Çoruh Valley of Turkey. The sampling areas were located between the coordinates 40°48'39.06" N - 41°31'37.49" E and 40°22'37.69" N - 40°28'13.82" E. In the preliminary screening phase, a total of 50 individuals were evaluated based on fruit weight, rind color (L*, a*, b*), total soluble solids (TSS, ≥14 °Brix), titratable acidity, and visual maturity. As a result of this preliminary evaluation, 15 promising genotypes exhibiting superior qualities were selected. All selected genotypes were naturally occurring wild individuals growing on privately owned land, and no cultivated orchards were included in the study. Harvesting was carried out in the morning (08:00-10:00), when the fruits were fully physiologically ripe. All samples were collected within the natural ripening window of late August to mid-September during the 2024 harvest season. Fruit collected from each individual was transported to the laboratory under cold chain conditions (4 °C, in ice-packed transport containers) within 2 hours after harvest.

Samples brought to the laboratory were prepared for analysis within 24 hours; they were stored at -20 °C prior to chemical and biochemical analyses and were evaluated immediately after thawing. Three biological replicates were applied for each genotype and three technical replicates for each biological replicate, resulting in a total sample size of n = 9.

Physicochemical analyses

Total Soluble Solids (TSS): Total soluble solids (TSS) content was determined in °Brix using a digital refractometer (Atago PAL-1, Japan; ± 0.1 °Brix) (AOAC, 2016).

Titratable Acidity (TA): Titratable acidity (TA) was calculated by diluting 10 g of homogenized fresh fruit sample with 100 mL of distilled water and titrating it with 0.1 N NaOH solution. Phenolphthalein indicator was used, and the endpoint was determined when the pink color persisted for at least 30 seconds. Results were expressed as g of malic acid per 100 g of fresh matter (AOAC, 2016).

pH Measurement: pH measurements were performed using a pH meter (Mettler Toledo S220-K) with ± 0.01 precision. The device was verified by three-point calibration with pH 4.01, 7.00, and 10.01 buffer solutions before each analysis.

All basic chemical analyses were conducted in triplicate, and results are reported as the mean ± standard deviation (SD).

Total and Reducing Sugar Content: Total and reducing sugar contents were determined using the DNS method of Miller (1959). Absorbance measurements were taken at 540 nm; a glucose standard curve was prepared in the range of 0-500 mg L^{-1}, and the accuracy of the calibration curve was confirmed with $R^2 = 0.998$.

Ascorbic Acid (Vitamin C): Ascorbic acid content was analyzed using the classical method based on titration with 2,6-dichlorophenolindophenol solution. Results are reported in mg/100 g of fresh matter (AOAC, 2016; Kalyoncu, 1996)

Total Tannin Content: Total tannin content was determined using the Folin-Denis spectrophotometric method. Measurements were performed at a wavelength of 700 nm, and the tannic acid standard curve (10-200 mg L^{-1}, $R^2 = 0.999$) was used. Results are given as mg TAE/100 g of fresh material (AOAC, 2016; Hagerman and Butler, 1978).

Organic acid analysis (HPLC)

Organic acid composition was determined using an Agilent 1260 Infinity II HPLC system (Agilent Technologies, Germany). A Rezex ROA-Organic Acid H^+ (8%) 300 × 7.8 mm column (Phenomenex, USA) was used for separation. The mobile phase was 0.005 N H_2SO_4 at a flow rate of 0.6 mL/min under isocratic conditions; the column temperature was set at 35 °C, the injection volume was set at 20 µL, and the detection wavelength was set at 220 nm. The total analysis time was 30 minutes, and sufficient peak separation was achieved for all organic acids.

During sample preparation, 5 g of fresh fruit was taken, homogenized with 25 mL of ultrapure water, and the mixture was centrifuged at 10,000 rpm for 15 minutes. The resulting supernatant was filtered through a 0.45 µm PVDF filter. 50 mg L^{-1} tartaric acid was added as an internal standard to all standard solutions and samples to increase the accuracy of quantitative analysis. Calibration curves were created with standard solutions ranging from 1 to 200 mg L^{-1}, and R^2 values > 0.999 were obtained for all organic acids. LOD-LOQ values were determined as 0.12 and 0.38 mg L^{-1} for malic acid and 0.09 and 0.30 mg L^{-1} for citric acid, respectively, and similar levels were observed for other acids. The accuracy of the method was confirmed with intra-day RSD values of 1.8-3.5% and inter-day RSD values of 2.3-4.7%. Recovery rates were found to range from 95.4% to 103.2%. Analyses were conducted in triplicate, and results were reported as mg/100 g of fresh matter, calculated from internal-standard-corrected peak areas (Karadeniz, 2004; Tural and Koca, 2008; AOAC, 2016)

Free amino acid analysis (HPLC-OPA/FMOC)

Free amino acid contents were analyzed using the OPA/FMOC derivatization method using an Agilent 1260 Infinity II HPLC system and a ZORBAX Eclipse AAA column. 5 g of fresh fruit samples from each genotype were homogenized with 0.1% HCl, centrifuged at 12,000 rpm for 20 minutes, and the resulting supernatant was filtered through a 0.22 µm PVDF filter. Primary amino acids were determined at 338 nm by derivatization with OPA, and secondary amino acids were determined at 262 nm by derivatization with

FMOC. Analysis conditions were optimized for a flow rate of 2.0 mL/min, a column temperature of 40 °C, an injection volume of 10 µL, and a total run time of 26 minutes. A 40 mM Na_2HPO_4 (pH 7.8) solution (A) and an ACN:MeOH:H_2O (45:45:10) mixture (B) were used as mobile phases.

20 µmol L^{-1} norvaline was used as an internal standard for quantification. Standard solutions were prepared for all amino acids in the range of 0.5-100 µmol L^{-1}, and high accuracy ($R^2 \geq 0.999$) was achieved in the calibration curves. LOD values were calculated as 0.01-0.08 µmol L^{-1} for primary amino acids and 0.05-0.12 µmol L^{-1} for secondary amino acids. Peak purity was verified by DAD spectral analysis, and method reproducibility was found to be in the range of 1.2-3.8% RSD.

All analyses were performed in triplicate, and results are reported in mg/100 g of fresh matter.

Statistical analyses

Statistical analyses were performed using SPSS 22.0 software (IBM Corp., Armonk, NY, USA). The distributional properties of the data were assessed using the Shapiro-Wilk normality test, and variance homogeneity was checked using the Levene test. One-way ANOVA was applied to parameters showing homogeneous variance; differences between means were determined using the Tukey HSD multiple comparison test ($p < 0.05$).

A Pearson correlation matrix was created to examine the relationships between physicochemical properties, organic acid composition, sugar profile, and free amino acid levels. Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were used for multivariate structural assessment; Ward's linkage method and Euclidean distance metric were used in HCA. Component loadings, variance contribution rates, and total explained variance were calculated in PCA, and graphs and tables for all multivariate analyses are presented in detail in the Results section.

Results

Physicochemical properties of genotypes

The basic physicochemical properties of cornelian cherry genotypes are presented in Table 1. The findings revealed statistically significant differences among genotypes in all parameters examined ($p < 0.05$). Overall, considerable genotypic variation was observed in soluble solids, acidity, sugars, vitamin C, pH, and tannin levels. TSS contents ranged from 14.34% to 25.61%, with genotypes G15, G9, G3, and G6 showing relatively higher values. Total acidity varied between 1.40% and 2.35%, and G8, G4, and G13 exhibited the highest acidity, while G6 and G15 had lower acidity values.

The TSS/acid ratio differed markedly among genotypes, and G4 and G12 showed the most balanced sweetness-acidity profiles.

Total sugar content ranged from 6.97% to 8.25%, and G12, G11, and G6 were the most sugar-rich genotypes. Reducing sugars also varied considerably, with G11 showing the highest values.

Vitamin C levels ranged from 55.42 to 73.59 mg/100 g, with G3, G7, G6, and G12 identified as the richest genotypes. pH values ranged between 2.52 and 2.87. Tannin content exhibited substantial variation (138.45-542.27 mg TAE/100 g), and G2, G14, and G13 contained notably higher tannin levels.

Taken together, these results demonstrate substantial biochemical and technological diversity among cornelian cherry genotypes, highlighting several individuals with favorable characteristics for either fresh consumption or industrial processing

Table 1. Physicochemical properties of different *C. mas* genotypes (mean ± SD)

Genotypes	TSS (°Brix)	Total Acid (%)	TSS / acid	Total sugar (%)	Reducing sugar (%)	Vitamin C (mg/100 g)	pH	Tannin (mg TAE/100 g)
G1	16.25 ± 0.18 d	1.85 ± 0.04 c	7.21 ± 0.05 c	7.12 ± 0.02 b	2.24 ± 0.02 a	48.38 ± 3.01 a	2.52 ± 0.02 a	148.58 ± 1.86 b
G2	17.83 ± 0.27 e	1.92 ± 0.03 c	9.12 ± 0.12 f	7.63 ± 0.17 e	4.59 ± 0.19 i	68.48 ± 0.87 f	2.71 ± 0.02 d	542.27 ± 3.96 l
G3	19.67 ± 0.13 g	1.87 ± 0.02 c	10.17 ± 0.09 h	6.98 ± 0.05 a	4.13 ± 0.08 g	57.56 ± 2.72 c	2.81 ± 0.00 f	431.24 ± 3.57 j
G4	16.24 ± 0.05 d	2.11 ± 0.02 d	12.38 ± 0.11 k	7.46 ± 0.05 cd	3.97 ± 0.09 f	63.71 ± 1.35 e	2.76 ± 0.04 e	367.54 ± 4.35 h
G5	18.56 ± 0.46 f	1.92 ± 0.03 c	11.27 ± 0.12 j	7.83 ± 0.08 f	2.58 ± 0.03 b	69.47 ± 2.19 g	2.69 ± 0.03 cd	412.56 ± 7.52 i
G6	19.61 ± 0.30 g	1.82 ± 0.00 b	9.59 ± 0.15 g	7.15 ± 0.10 c	3.74 ± 0.06 e	71.57 ± 1.35 hi	2.87 ± 0.05 g	183.94 ± 5.72 d
G7	14.34 ± 0.19 a	1.96 ± 0.04 c	8.62 ± 0.08 d	7.94 ± 0.07 fg	3.69 ± 0.04 de	72.34 ± 2.31 i	2.69 ± 0.11 cd	254.42 ± 4.37 f
G8	15.29 ± 0.19 b	2.35 ± 0.09 e	6.93 ± 0.14 b	6.97 ± 0.08 a	2.87 ± 0.11 c	57.85 ± 1.59 c	2.63 ± 0.00 bc	163.75 ± 2.16 c
G9	22.24 ± 0.53 h	2.15 ± 0.19 d	6.31 ± 0.08 a	7.16 ± 0.10 bc	3.69 ± 0.18 de	72.26 ± 1.49 hi	2.72 ± 0.02 de	317.57 ± 5.41 g
G10	21.95 ± 0.27 h	1.84 ± 0.14 d	7.38 ± 0.08 c	7.28 ± 0.21 cd	4.27 ± 0.19 h	59.68 ± 0.98 d	2.82 ± 0.03 f	412.34 ± 3.78 i
G11	17.68 ± 0.31 e	1.89 ± 0.25 c	11.24 ± 0.16 j	8.12 ± 0.18 g	5.67 ± 0.08 j	63.46 ± 0.97 e	2.78 ± 0.04 ef	167.54 ± 7.52 c
G12	18.64 ± 0.45 f	1.92 ± 0.01 c	12.37 ± 0.17 k	8.25 ± 0.10 h	5.55 ± 0.09 j	71.34 ± 2.57 h	2.64 ± 0.01 bc	217.68 ± 4.69 e
G13	15.67 ± 0.09 c	2.14 ± 0.06 d	11.56 ± 0.12 j	7.56 ± 0.03 e	3.57 ± 0.14 d	52.56 ± 2.19 b	2.63 ± 0.05 bc	437.64 ± 7.56 j
G14	19.72 ± 0.37 g	1.97 ± 0.09 c	9.87 ± 0.18 g	7.87 ± 0.05 f	4.29 ± 0.14 h	57.89 ± 1.21 c	2.66 ± 0.07 c	512.34 ± 5.37 k
G15	25.61 ± 0.22 i	1.40 ± 0.07 a	8.95 ± 0.09 e	7.92 ± 0.11 f	5.63 ± 0.13 j	72.34 ± 0.87 i	2.69 ± 0.03 cd	138.45 ± 6.25 a

*SS: total soluble solids (°Brix); total acidity: titratable acidity as malic acid (%); TSS/Acid: TSS (°Brix)/total acidity ratio; total and reducing sugars: DNS method; vitamin C: ascorbic acid determined by 2,6-dichlorophenolindophenol titration method (mg/100 g fresh matter); pH: measured with a Mettler Toledo S220-K pH meter; tannin: tannic acid equivalent (mg TAE/100 g) by the Folin-Denis spectrophotometric method. Values are given as mean ± standard deviation (n = 3). Means with different letters in the same column are statistically different according to the Tukey HSD test ($p < 0.05$)

Organic acid profiles of genotypes

The organic acid compositions of the cornelian cherry genotypes are presented in Table 2. Analysis results revealed statistically significant differences among all organic acid components ($p < 0.05$). Malic acid was the predominant organic acid in every genotype, although the amount varied widely among individuals.

Table 2. Organic acid composition of cornelian *C. mas* genotypes (mean ± SD)

Genotype	Malic acid	Citric acid	Lactic acid	Fumaric acid	Oxalic acid	Ascorbic acid	Total organic acid
G1	243.31 ± 5.64 c	235.23 ± 4.09 b	135.73 ± 2.81 d	327.25 ± 5.25 a	34.27 ± 0.82 bc	62.36 ± 1.15 de	1038.15 ± 25.41 a
G2	251.34 ± 5.56 c	260.46 ± 0.93 a	39.69 ± 2.90 d	256.24 ± 4.65 c	38.12 ± 0.77 b	57.98 ± 0.96 f	909.16 ± 23.83 b
G3	174.34 ± 3.43 e	178.21 ± 1.25 c	135.73 ± 3.26 d	317.28 ± 3.24 b	39.23 ± 1.23 b	73.59 ± 1.23 a	918.38 ± 26.85 b
G4	214.12 ± 9.83 d	149.27 ± 3.54 d	56.24 ± 0.63 g	237.28 ± 8.96 d	47.68 ± 0.57 a	63.27 ± 2.13 d	767.86 ± 53.64 d
G5	187.24 ± 7.20 e	67.39 ± 4.32 g	237.31 ± 0.96 b	246.71 ± 7.92 c	57.28 ± 1.03 a	68.14 ± 0.87 b	864.07 ± 29.31 c
G6	167.37 ± 11.12 e	189.22 ± 1.39 c	37.28 ± 3.25 h	198.37 ± 2.44 e	45.18 ± 1.67 a	71.38 ± 0.19 a	708.80 ± 22.12 e
G7	245.31 ± 9.32 c	187.24 ± 1.24 c	53.27 ± 1.43 g	34.27 ± 0.97 h	22.34 ± 0.27 d	72.16 ± 1.26 a	595.59 ± 15.63 f
G8	57.28 ± 6.89 g	145.37 ± 8.16 b	163.37 ± 0.63 c	198.37 ± 1.58 e	18.69 ± 2.20 d	70.91 ± 0.96 a	741.99 ± 17.56 d
G9	211.34 ± 1.32 d	21.31 ± 2.47 h	214.12 ± 0.46 b	185.38 ± 8.54 e	34.27 ± 0.32 bc	68.56 ± 0.28 b	734.98 ± 18.69 d
G10	214.12 ± 12.25 d	18.69 ± 2.64 h	223.12 ± 2.36 b	195.29 ± 3.69 e	35.19 ± 2.24 bc	69.67 ± 1.26 b	755.08 ± 25.86 d
G11	199.37 ± 4.23 d	135.73 ± 3.56 e	21.31 ± 3.14 i	123.65 ± 4.57 f	41.24 ± 0.96 b	67.59 ± 1.11 b	588.89 ± 16.86 f
G12	187.47 ± 8.95 e	23.65 ± 7.30 h	217.52 ± 1.42 b	135.73 ± 5.61 f	34.27 ± 1.23 bc	70.15 ± 0.89 a	668.79 ± 13.96 e
G13	56.24 ± 2.18 g	136.77 ± 1.38 e	38.12 ± 0.79 h	371.49 ± 6.35 a	42.37 ± 0.49 b	55.42 ± 1.11 f	700.41 ± 19.12 e
G14	187.24 ± 11.25 e	22.34 ± 4.16 h	23.65 ± 0.88 i	334.87 ± 1.22 b	69.27 ± 1.18 a	66.12 ± 0.85 c	703.49 ± 18.63 e
G15	38.12 ± 2.60 h	176.28 ± 3.85 c	175.28 ± 1.69 c	167.43 ± 2.13 e	48.79 ± 0.51 a	63.75 ± 1.26 d	669.65 ± 21.23 e
Significance (*p*)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

* Values are given as mean ± standard deviation (n = 3). Differences between values indicated with different letters in the same column are statistically significant ($p < 0.05$) according to the Tukey HSD test. Organic acid analyses were performed on an Agilent 1260 Infinity II HPLC system using a Rezex ROA-Organic Acid H^+ (8%) column

Malic acid ranged from 38.12 to 251.34 mg/100 g, and G2, G7, and G1 showed the highest concentrations, while G13 and G15 contained the lowest levels. Citric acid also differed considerably (18.69-260.46 mg/100 g), and G2 and G1 were the richest genotypes. Lactic acid varied substantially (21.31-237.31 mg/100 g), with G5, G9, and G10 showing higher levels. Fumaric acid ranged from 34.27 to 371.49 mg/100 g, with G13, G14, and G1 exhibiting elevated concentrations. Oxalic acid values ranged between 18.69 and 69.27 mg/100 g, and G14, G5, and G4 contained the highest amounts.

Ascorbic acid levels showed moderate variation among genotypes, ranging from 55.42 to 73.59 mg/100 g, and G3, G6, G7, and G8 contained the highest vitamin C levels. Total organic acids ranged between 588.89 and 1038.15 mg/100 g, with G1, G2, and G3 identified as the most organic-acid-rich genotypes.

Overall, the pronounced variation in organic acid profiles suggests strong genotypic differentiation within the population.

Free amino acid profiles of genotypes

The free amino acid contents of the cornelian cherry genotypes are presented in Table 3. Analyses showed statistically significant differences among genotypes for all amino acid components ($p < 0.001$). Overall, substantial genotypic variation was observed in both individual amino acids and total free amino acid content.

Table 3. Amino acid contents of *C.-mas* genotypes (mg/100 g, HPLC results)

Genotypes	Leucine	Lysine	Threonine	Phenylalanine	Isoleucine	Methionine	Tryptophan	Histidine	Valine	Total Free Amino Acids
G1	10.09 ± 0.131 g	2.71 ± 0.149 b	6.72 ± 0.320 f	12.64 ± 0.652 i	12.39 ± 0.185 I	13.84 ± 0.301 h	8.40 ± 0.275 a	10.43 ± 0.919 m	6.90 ± 0.330 a	84.27 ± 3.300 g
G2	6.39 ± 0.245 b	7.66 ± 0.124 j	9.89 ± 0.328 k	12.77 ± 0.091 j	5.49 ± 0.292 c	9.35 ± 0.230 b	15.60 ± 1.007 g	9.48 ± 1.546 h	11.07 ± 0.366 I	87.72 ± 3.949 l
G3	6.57 ± 0.186 c	8.62 ± 0.057 m	10.01 ± 0.266 m	3.01 ± 0.185 e	11.77 ± 0.165 h	14.73 ± 0.288 I	12.03 ± 0.290 c	9.54 ± 0.694 j	10.43 ± 0.473 g	86.89 ± 1.801 j
G4	11.32 ± 0.253 j	8.42 ± 0.164 l	8.32 ± 0.249 j	2.80 ± 0.204 d	12.69 ± 0.267 k	8.79 ± 0.259 a	17.30 ± 0.724 k	8.14 ± 1.029 c	7.70 ± 0.952 c	87.24 ± 3.331 k
G5	8.62 ± 0.117 d	4.08 ± 0.133 f	7.73 ± 0.301 h	2.40 ± 0.252 a	13.27 ± 0.183 l	19.02 ± 0.337 k	17.36 ± 0.268 l	7.66 ± 1.850 b	10.48 ± 0.402 h	92.64 ± 5.058 n
G6	10.43 ± 0.205 h	3.17 ± 0.469 c	8.23 ± 0.126 I	12.95 ± 0.156 k	5.18 ± 0.025 b	13.19 ± 0.272 f	13.42 ± 0.193 f	8.89 ± 0.506 g	10.46 ± 0.522 g	85.91 ± 4.118 h
G7	11.12 ± 0.304 k	2.63 ± 0.084 a	6.84 ± 0.673 g	10.52 ± 0.169 h	12.45 ± 0.086 j	13.39 ± 0.212 g	16.16 ± 0.297 i	8.45 ± 0.573 e	11.14 ± 0.334 I	93.14 ± 1.634 o
G8	11.25 ± 0.229 i	3.50 ± 0.346 e	3.42 ± 0.472 b	2.73 ± 0.089 c	11.64 ± 0.174 g	16.47 ± 0.288 j	12.95 ± 0.761 e	7.19 ± 0.906 a	10.34 ± 0.168 f	79.52 ± 1.537 d
G9	4.70 ± 0.410 a	6.92 ± 0.245 h	9.99 ± 0.341 l	10.29 ± 0.273 g	10.09 ± 0.540 f	9.61 ± 0.233 c	15.77 ± 1.332 h	10.24 ± 0.617 n	8.87 ± 0.729 e	86.77 ± 4.978 I
G10	6.31 ± 0.245 b	7.16 ± 0.124 j	9.89 ± 0.328 k	13.12 ± 0.091 l	5.48 ± 0.292 c	9.35 ± 0.230 b	15.12 ± 1.007 g	9.40 ± 1.546 I	11.09 ± 0.366 I	88.04 ± 3.949 m
G11	6.57 ± 0.186 c	4.79 ± 0.104 g	10.21 ± 0.266 m	3.11 ± 0.185 e	5.19 ± 0.332 b	10.31 ± 0.285 d	11.03 ± 0.290 c	9.39 ± 0.694 k	10.46 ± 0.473 g	72.02 ± 3.975 c
G12	9.96 ± 0.232 f	8.17 ± 0.164 l	3.12 ± 0.372 a	2.46 ± 0.204 d	12.68 ± 0.267 k	8.29 ± 0.259 a	16.11 ± 0.724 k	8.19 ± 1.029 d	7.61 ± 0.952 c	80.97 ± 3.779 e
G13	9.83 ± 0.162 e	3.41 ± 0.346 d	3.52 ± 0.192 c	2.62 ± 0.245 b	7.73 ± 0.232 e	14.13 ± 0.288 I	12.77 ± 0.678 d	9.82 ± 0.906 l	7.11 ± 0.183 b	71.65 ± 3.770 b
G14	10.23 ± 0.205 h	7.52 ± 0.362 i	5.31 ± 0.177 e	3.61 ± 0.130 f	4.52 ± 0.177 a	12.19 ± 0.272 f	16.33 ± 0.749 j	10.74 ± 0.499 o	10.12 ± 0.522 g	81.12 ± 4.514 f
G15	11.48 ± 0.304 k	8.37 ± 0.194 k	4.00 ± 0.139 d	3.10 ± 0.316 e	5.92 ± 0.335 d	11.47 ± 0.297 e	10.23 ± 0.536 b	8.74 ± 1.309 f	7.92 ± 0.465 d	71.34 ± 1.572 a
Significance (*p*)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

* Values are given as mean ± standard deviation (n = 3). Differences between values indicated with different letters in the same column are statistically significant ($p < 0.05$) according to the Tukey HSD test. Amino acid analyses were carried out by the OPA/FMOC derivatization method on a ZORBAX Eclipse AAA column (4.6 × 250 mm, 5 μm) using an HPLC system (Agilent 1260 Infinity II)

Leucine ranged from 6.31 to 11.48 mg/100 g, with G7, G8, G15, and G4 identified as the richest genotypes. Lysine showed a wide range (2.63-8.62 mg/100 g), and G3, G12, G4, and G15 exhibited the highest levels.

Threonine values varied from 3.12 to 10.21 mg/100 g, and G2, G3, G9, G10, and G11 contained higher amounts. Phenylalanine ranged from 2.40 to 13.12 mg/100 g, with G10, G1, G2, and G6 showing elevated concentrations. Isoleucine values (4.52-13.27 mg/100 g) differed markedly among genotypes, and G7, G4, G12, and G1 were the richest genotypes. Methionine ranged between 8.29 and 19.02 mg/100 g; G13, G8, and G3 contained comparatively higher levels.

Tryptophan values varied from 8.40 to 17.36 mg/100 g, with G4, G7, G12, and G14 showing the highest concentrations. Histidine values showed moderate variation (7.19-10.74 mg/100 g), and G1 and G9 exhibited

higher levels. Valine ranged from 6.90 to 11.14 mg/100 g, with G7, G2, and G10 identified among the richest genotypes.

Total free amino acid contents ranged from 71.34 to 93.14 mg/100 g, and G7, G5, G10, and G2 contained the highest totals.

These results indicate pronounced biochemical differentiation among genotypes, reflecting strong genetic variation in amino acid metabolism.

Multivariate statistical analyses (PCA and HCA)

In this study, PCA and HCA were applied to evaluate the relationships between the physicochemical properties, organic acid composition, and free amino acid profiles of the genotypes. The first two principal components (PC1 and PC2) explained a substantial proportion of the total variance, allowing clear separation among genotypes based on their biochemical traits (Figure 1). Genotypes such as G3, G5, and G7 were positioned distinctly along PC1 due to their higher organic acid and amino acid contents, whereas G9, G11, and G12 grouped more closely along PC2, reflecting their relatively balanced physicochemical profiles. The HCA dendrogram classified the genotypes into clusters consistent with PCA results (Figure 2). One major cluster included G9, G11, and G12, characterized by moderate acidity and higher sugar levels, while another cluster comprising G3, G5, and G7 was associated with elevated organic acids and amino acids. Overall, the clustering pattern confirmed the biochemical differentiation among the evaluated genotypes.

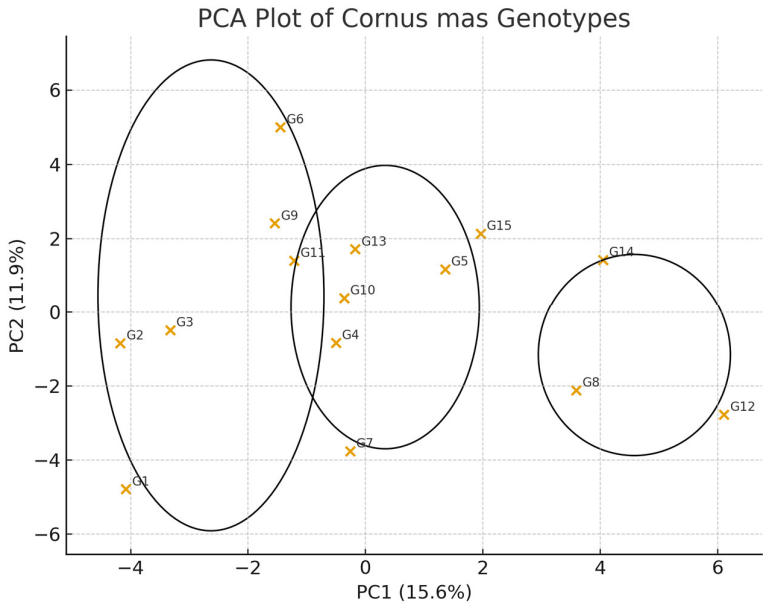

Figure 1. Principal Component Analysis (PCA) of 15 *C. mas* genotypes based on standardized physicochemical properties, organic acid composition, and free amino acid profiles. PC1 (15.6%) and PC2 (11.9%) together explained 27.5% of the total variance

The distribution of genotypes formed three distinct clusters: (1) a left cluster (G1, G2, G3, G6, G9, G11) associated with lower PC1 scores and wider variation along PC2, (2) a central cluster (G4, G7, G10, G13, G5, G15) showing balanced biochemical traits, and (3) a right cluster (G8, G14, G12) characterized by high PC1 values. This clear group separation indicates strong biochemical differentiation among genotypes and supports the grouping patterns observed in the HCA dendrogram

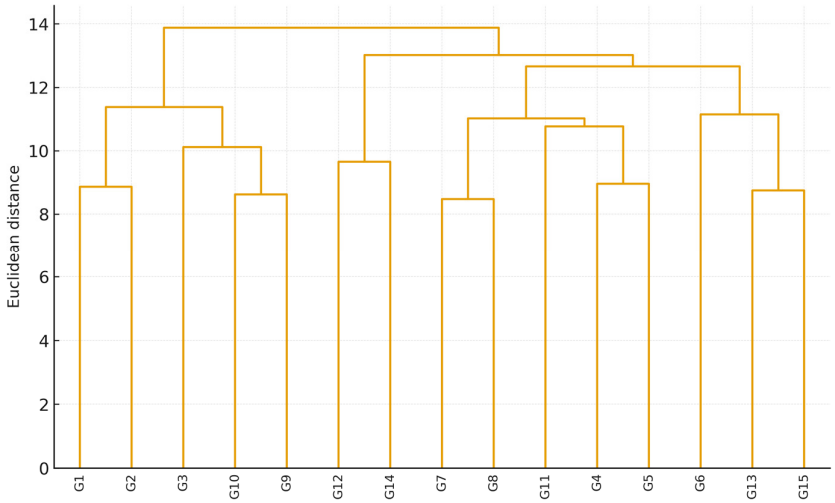

Figure 2. Hierarchical Cluster Analysis (HCA) of 15 *C. mas* genotypes using Ward's method and Euclidean distance

The dendrogram revealed three major genotype clusters, consistent with the PCA results. Cluster I consisted of G1, G2, G3, G10, and G9, representing genotypes with relatively low PC1 scores and moderate physicochemical variation. Cluster II included G12, G14, G7, G8, G11, and G4, forming a central group characterized by balanced biochemical traits. Cluster III comprised G5, G6, G13, and G15, which displayed higher PC1 values and distinct organic acid-amino acid profiles. The agreement between PCA and HCA confirms the strong biochemical differentiation among the genotypes

Discussion

This study revealed wide variation in the physicochemical properties, organic acid, and free amino acid compositions of 15 cornelian cherry genotypes naturally growing in the Çoruh Valley. Significant differences ($p < 0.05$) between genotypes in all biochemical parameters indicate that the region is an important center of genetic diversity for cornelian cherry. These findings confirm that environmental heterogeneity and genetic background strongly influence fruit biochemical composition.

Physicochemical properties

TSS values showed considerable variation among genotypes, consistent with reports that soluble solids are strongly genotype-dependent (Antoniewska-Krzeska *et al*., 2022). Genotypes with higher TSS and favorable TSS/TA ratios are generally more suitable for fresh consumption, which aligns with earlier studies identifying sweetness-acidity balance as a key sensory determinant (Yilmaz *et al*., 2009). In the present study, certain genotypes demonstrated such balanced profiles, supporting their potential use in fresh-market applications.

Organic acid composition

The predominance of malic acid in all genotypes aligns with previous studies on the species (Tural and Koca, 2008). The large inter-genotype variation in both malic and citric acid indicates that organic acid metabolism is strongly genetically regulated. Genotypes characterized by higher total organic acid levels may be more suitable for processing applications where acidity contributes to product stability, flavor structure, and shelf-life. Differences in fumaric and oxalic acid contents are also consistent with earlier reports and highlight the biochemical diversity of *C. mas* (Szczepaniak *et al*., 2019).

Free amino acid content

Although studies on the amino acid composition of cornelian cherry remain limited, available reports confirm that amino acid levels exhibit genotypic variation (Antoniewska-Krzeska *et al*., 2022). The considerable differences observed in amino acids such as leucine, isoleucine, phenylalanine, and tryptophan indicate differential activity of nitrogen-related metabolic pathways among genotypes. Genotypes with higher total free amino acid contents may therefore serve as valuable raw materials for functional food or nutraceutical development.

Genotypic differentiation and industrial relevance

The results demonstrate that cornelian cherry genotypes vary widely in their suitability for different uses. Some genotypes showed biochemical characteristics compatible with fresh-market consumption, while others exhibited properties more suitable for processed products requiring higher acidity or elevated amino acid content. Such differentiation is consistent with multi-criteria evaluation approaches reported by (Skender *et al*., 2022). The findings also support ecological genetic models noting that populations in heterogeneous environments accumulate higher biochemical diversity (Jump and Peñuelas, 2005).

Overall, the biochemical variability observed in this study confirms that the Çoruh Valley hosts valuable genetic resources that may contribute to future breeding programs aimed at quality improvement, stress adaptation, and functional food development.

Conclusion

This study revealed a wide biochemical variation in the physicochemical properties, organic acid, and free amino acid profiles of 15 cornelian cherry genotypes selected from the Çoruh Valley. Significant genotypic differences ($p < 0.05$) in all parameters confirmed that the region is a center of high genetic diversity for cornelian cherry. Malic acid was determined to be the dominant organic acid in all genotypes, reflecting the species' metabolic characteristics. The substantial variability observed in total organic acids, sugars, vitamin C, and amino acids demonstrates that genotypes differ markedly in their technological and nutritional potential. Certain genotypes exhibited biochemical features suitable for fresh consumption, while others showed characteristics more appropriate for processing or functional food applications. Overall, the results highlight the importance of the Çoruh Valley as a valuable genetic reservoir for future breeding efforts and quality-oriented selection programs.

Authors' Contributions

Conceptualization: ÜE and YE; Methodology: ÜE; Investigation: ÜE and YE; Data curation: ÜE and YE; Statistical analysis and validation: YE; Visualization: ÜE; Writing-original draft: ÜE; Writing - review & editing: ÜE and YE; Supervision and administration: YE and ÜE.

All authors have read and approved the final version of the manuscript.

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Conflict of Interests

The authors declare that there are no conflicts of interest related to this article.

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