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Original Article

Trend of phytochemical composition changes of *Sorbus aucuparia* l. depending on the season in the conditions of the Ili Alatau

Tendência das mudanças na composição fitoquímica de *Sorbus aucuparia* L. em função da estação nas condições do Ile Alatau

A. Artykbay[a*], N. Akhtayeva[a*], G. Ultanbekova[a], D. Abdildanov[a,b], H. Toktay[c], K. Dlafruz[d] and S. Ussen[a,b]

[a]Al-Farabi Kazakh National University, Faculty of Biology and Biotechnology, Almaty, Kazakhstan
[b]Institute of Botany and Phytointroduction, Laboratory of Flora of Higher Plants, Almaty, Kazakhstan
[c]University of Nigde Omer Halisdemir University, Department of Plant Production, Nigde, Turkey
[d]Tashkent Pharmaceutical Institute, Department of Uzbek Language and Literature, Tashkent, Uzbekistan

Abstract

This study investigates the seasonal variation in the phytochemical composition of rowan (*Sorbus aucuparia* L.) fruit extracts collected during the summer and autumn vegetation periods. Gas chromatography–mass spectrometry (GC–MS) was employed to characterize qualitative and quantitative changes in individual compounds and compound classes associated with fruit ripening and metabolic adaptation. The summer extracts were dominated by secondary metabolites, primarily lactones and furan derivatives, with dihydro-3-methylene-5-methyl-2-furanone and 5-hydroxymethylfurfural representing the major constituents. Their elevated levels indicate intensive carbohydrate transformation and active metabolic processes during early fruit development. In contrast, the autumn samples exhibited a pronounced accumulation of primary metabolites, particularly polyols (sorbitol, 1,4-anhydro-D-galactitol, mannitol) and fatty acids, including *n*-hexadecanoic (palmitic) and unsaturated fatty acids. This metabolic shift reflects physiological maturation and preparation for overwintering, accompanied by enhanced energy storage and osmoprotective mechanisms. Comparative analysis revealed a significant decrease in lactones and furans alongside a substantial increase in sugar alcohols and lipid components in autumn fruits. Visualization techniques, including dumbbell, lollipop, grouped bar, and sunburst charts, highlighted a fundamental restructuring of the metabolome from volatile and reactive compounds toward more stable constituents. Overall, the results demonstrate that harvest season plays a critical role in determining the chemical profile and functional properties of *Sorbus aucuparia* fruits, which is essential for their targeted use in food, pharmaceutical, and nutraceutical applications.

Keywords: black chokeberry (*Sorbus aucuparia* L.), gas chromatography, seasonal variation, furan compounds, antioxidants.

Resumo

Este estudo investiga a variação sazonal na composição fitoquímica de extratos de frutos de sorveira (*Sorbus aucuparia* L.) coletados durante os períodos de vegetação de verão e outono. A cromatografia gasosa acoplada à espectrometria de massas (GC–MS) foi empregada para caracterizar mudanças qualitativas e quantitativas em compostos individuais e classes de compostos associadas ao amadurecimento dos frutos e à adaptação metabólica. Os extratos de verão foram dominados por metabólitos secundários, principalmente lactonas e derivados de furano, sendo o di-hidro-3-metileno-5-metil-2-furanona e o 5-hidroximetilfurfural representando os principais constituintes. Seus níveis elevados indicam intensa transformação de carboidratos e processos metabólicos ativos durante o desenvolvimento inicial dos frutos. Em contraste, as amostras de outono apresentaram um acúmulo pronunciado de metabólitos primários, particularmente polióis (sorbitol, 1,4-anidro-D-galactitol, manitol) e ácidos graxos, incluindo o ácido n-hexadecanoico (palmítico) e ácidos graxos insaturados. Essa mudança metabólica reflete a maturação fisiológica e a preparação para o inverno, acompanhadas por maior armazenamento de energia e mecanismos osmoprotetores. A análise comparativa revelou uma diminuição significativa de lactonas e furanos, com aumento substancial de álcoois de açúcar e componentes lipídicos nos frutos de outono. Técnicas de visualização, incluindo gráficos do tipo *dumbbell*, *lollipop*, barras agrupadas e *sunburst*, destacaram uma reestruturação fundamental do metaboloma, passando de compostos voláteis e reativos para constituintes mais estáveis. De modo geral, os resultados demonstram que a estação de colheita desempenha um papel crucial na determinação do perfil químico e das propriedades funcionais dos frutos de *Sorbus aucuparia*, o que é essencial para seu uso direcionado em aplicações alimentícias, farmacêuticas e nutracêuticas.

Palavras-chave: sorveira (*Sorbus aucuparia* L.), cromatografia gasosa, variação sazonal, compostos de furano, antioxidantes.

*e-mail: akhtaeva@mail.ru; muratkyzyakbilek@gmail.com
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1. Introduction

Sorbus aucuparia L. (rowan, or European mountain ash) is a deciduous tree widely distributed across most of Europe and valued for its nutritional and medicinal properties. Rowan fruits (berries) represent a rich source of vitamins, polysaccharides, organic acids, and mineral constituents, and their high nutritional value has been well documented (Zlobin et al., 2012). Following processing, the fruits are commonly consumed in the form of jams, jellies, juices, syrups, and alcoholic beverages (including wines, bitters, and liqueurs) (Facciola, 1998).

In addition, rowan berries serve as a source of natural dietary polyphenols, which are frequently associated with the prevention of so-called civilization-related diseases (Tangney and Rasmussen, 2013). Rowan is also a traditional medicinal plant, primarily used in the management of diabetes mellitus and the prevention of its cardiovascular complications (Shikov et al., 2014). However, the mechanisms underlying the biological activity and the phytochemical composition of rowan fruits remain insufficiently elucidated.

Previous studies have demonstrated the ability of rowan berries to inhibit enzymes involved in the digestion of complex carbohydrates, namely α-amylase and α-glucosidase. Fractions enriched in chlorogenic acids and proanthocyanidins exhibited the highest inhibitory activity (Grussu et al., 2011; Boath et al., 2012). Furthermore, the efficacy of the berries in reducing blood glucose levels and improving insulin resistance has been confirmed in vivo in a murine model of diabetes (Wei et al., 2016).

The pronounced antioxidant activity of rowan fruits—exceeding that of many commonly consumed fruits, including apples, cherries, plums, strawberries, and blueberries—is considered one of the key contributors to their health-promoting effects. However, to date, this activity has been investigated in a limited number of chemical models, primarily involving assays based on the scavenging of synthetic free radicals (Olszewska and Michel, 2009; Kähkönen et al., 2001; Aladedunye and Matthäus, 2014; Mlcek et al., 2014;).

At the same time, oxidative stress is recognized as a major factor in the pathogenesis of diabetes mellitus and its complications, particularly those affecting the cardiovascular system (Volpe et al., 2018). It is generally accepted that one of the principal sources of reactive oxygen species (ROS) under hyperglycemic conditions is advanced glycation end products (AGEs). These heterogeneous compounds directly impair protein function and exacerbate oxidative stress by increasing intracellular ROS production (Nowotny et al., 2015; Volpe et al., 2018). The resulting oxidants damage functional biomolecules in blood plasma, vascular endothelium, vascular smooth muscle cells, and myocardium, leading to further cellular and tissue injury (Vinten-Johansen, 2004; Pacher and Szabo, 2006;).

In this context, the effects of bioactive constituents of rowan fruits on protein glycation processes, as well as their protective activity against ROS-induced damage *in vivo*, should be considered as potential mechanisms underlying their pharmacological effects.

The chemical composition of plant extracts is highly complex, and their biological properties may result from the combined action of multiple constituents exhibiting additive and synergistic effects (Rutkowska et al., 2019). In the case of rowan fruits, available data on their phytochemical profile and biological activity vectors remain incomplete. According to previous studies, the principal bioactive constituents of rowan fruits are polyphenols, including proanthocyanidins, caffeoylquinic acids, and flavonols; however, significant qualitative and quantitative discrepancies exist among reports (Abdel-Aty et al., 2019; Bujor et al., 2019; Bobinaitė et al., 2020).

Thus, qualitative analyses have identified between 13 and 36 polyphenolic compounds in rowan berries, including up to 7 oligomeric procyanidins, 4–9 hydroxycinnamic acid derivatives, and 2–13 flavonols, depending on the analytical method, geographical origin of the fruits, sample preparation procedures, and extract type. However, according to our preliminary data, the chemical composition of rowan fruits is considerably more complex, and its comprehensive characterization requires detailed investigation using LC–MS/MS analysis of separated and concentrated phenolic fractions obtained by fractionated extraction.

Moreover, the identification of compounds with diverse physicochemical properties (e.g., monomeric, oligomeric, and polymeric proanthocyanidins) necessitates the application of a combination of profiling techniques, including LC–MS/MS and UV spectrophotometric methods.

2. Materials and Methods

2.1. Material collection and morphological evaluation

To assess the phytochemical activity of *Sorbus aucuparia* fruits and to identify seasonal variations, plant material was collected twice: in early June and in late September. After harvesting, the fruits were air-dried at room temperature in shaded conditions until a constant mass was achieved, minimizing the risk of enzymatic degradation.

For morphological analysis, no fewer than 100 fruits were sampled and measured using a laboratory analytical microscope and balance (Levenhuk DTX RC4 5–270×). The obtained measurements were averaged arithmetically and used for subsequent analysis. Morphological characteristics of the fruits were examined and documented using light microscopy (Levenhuk DTX RC4 5–270×) and scanning techniques with a Microtek ObjectScan 1600 scanner.

2.2. Extract preparation and analysis

Prior to GC–MS analysis, the dried fruits were finely ground using a laboratory mill. The powdered samples were subjected to ultrasonic-assisted extraction with 70% ethanol at a solid-to-liquid ratio of 1:10 (w/v) for 30 minutes at 40 °C. The extracts were then filtered and concentrated under reduced pressure using a rotary evaporator. The concentrated samples were stored at +4 °C until further chromatographic examination.

2.3. GC–MS analysis and data processing

Gas chromatography–mass spectrometry (GC–MS) analysis was carried out using an Agilent 6890 gas chromatograph coupled with a 5973N mass selective detector (Agilent Technologies, USA) and equipped with a Combi-PAL autosampler (CTC Analytics AG, Switzerland). The autosampler system included a 32-position tray for 10/20 mL vials, an agitator, an SPME fiber holder, and a conditioning station.

The GC system was operated with a split/splitless injector in splitless mode. Separation of compounds was achieved on a DB-1MS capillary column (30 m × 0.25 mm, film thickness 0.25 µm; Agilent, USA). Helium served as the carrier gas at a constant flow rate of 1.0 mL/min.

The oven temperature program started at 40 °C with a 10-minute hold, followed by an increase to 240 °C at a rate of 20 °C/min, and a final hold at 240 °C for 20 minutes. The MS interface temperature was maintained at 240 °C. Mass spectra were recorded in full scan mode over an m/z range of 34–600.

Data analysis involved evaluation of retention times, peak areas, and interpretation of the acquired mass spectra. Identification of compounds was performed by matching the spectra with reference data from the Wiley 8th Edition and NIST'11 libraries, which together comprise over 700,000 reference mass spectra (Ussen et al., 2025).

3. Results

3.1. Morphology

Sorbus aucuparia L. (rowan tree, mountain ash) is a perennial deciduous tree or large shrub of the Rosaceae family, widely distributed across Europe, Western Asia, and parts of Siberia, and commonly found in mountainous and forested regions. The plant typically reaches 5–15 m in height, occasionally up to 20 m, with a slender trunk, smooth grayish bark, and a well-developed, moderately deep root system. Young shoots are pubescent and grayish-brown, becoming glabrous and darker with age.

The leaves are alternate, imparipinnate, 10–25 cm long, consisting of 9–19 lanceolate to oblong leaflets, each 3–7 cm long with sharply serrated margins. The upper surface of the leaflets is dark green, while the underside is lighter and slightly pubescent. In autumn, the foliage turns yellow, orange, or reddish tones, contributing to the high ornamental value of the species.

The inflorescences are dense, flat-topped corymbs bearing 80–250 small, white, bisexual flowers. Each flower possesses five petals, numerous stamens (15–25), and a superior ovary. Flowering occurs in May–June and is often accompanied by a characteristic strong scent. Pollination is predominantly entomophilous.

The fruits are small globose to ovoid pomes, 6–10 mm in diameter, bright orange to red at maturity, grouped in large clusters. Each fruit contains 2–5 small brown seeds. The flesh is juicy but markedly astringent and bitter when fresh due to the presence of organic acids, tannins, and phenolic compounds. Fruit ripening takes place from August to September, and the fruits often remain on the tree throughout winter, serving as an important food source for birds.

Sorbus aucuparia is characterized by high frost resistance, ecological plasticity, and tolerance to a wide range of soil and climatic conditions. Owing to its rich phytochemical composition and adaptability, the species is widely used in ornamental landscaping, traditional medicine, and as a source of bioactive compounds for food and pharmaceutical applications (Figure 1, Table 1).

Figure 1. Morphology of rowan fruits.

Table 1. Morphometric characteristics of rowan fruit.

No.	Parameter	Unit	Average Range (Normal)	Description and Notes
1	Fruit Length (Height)	mm	8.0 – 11.5	Vertical distance from the base to the apex.
2	Fruit Diameter (Width)	mm	7.5 – 10.5	Maximum horizontal measurement of the fruit.
3	Shape Index	ratio	0.9 – 1.1	Ratio of length to width (indicates globose to oval shape).
4	Weight of 100 Fruits	g	35.0 – 60.0	Indicator of fruit size and succulence.
5	Number of Seeds	pcs	1 – 5	Usually 2–3 well-developed seeds per pome.
6	Seed Length	mm	3.5 – 4.5	Seeds are typically elongated with a pointed apex.
7	Pedicel Length	mm	2.5 – 5.0	The stalk connecting the fruit to the corymb.
8	Pulp Content	%	65 – 80	The weight percentage of the succulent mesocarp.

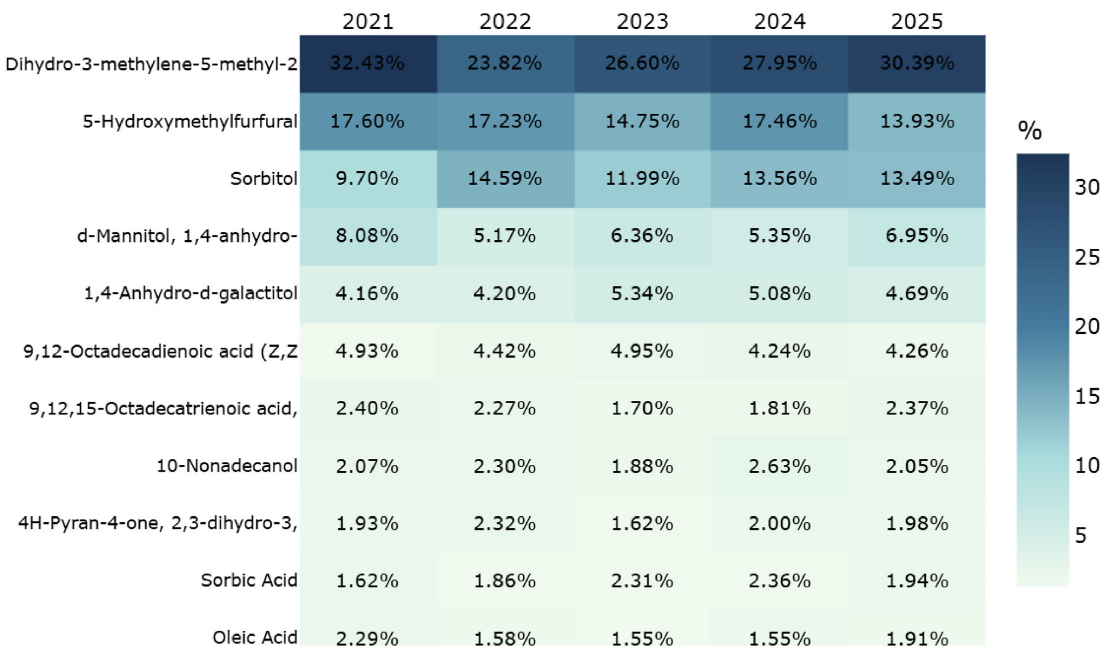

Figure 2. Heatmap of top compounds in rowan (2021–2025).

3.2. Dynamics of changes in phytochemical composition of Sorbus aucuparia L. (2021–2025)

The dynamics of the phytochemical composition of *Sorbus aucuparia* L. fruits over the period 2021–2025 are characterized by the presence of a stable dominant component, relative stability of key metabolites, and moderate variability of minor constituents (Figure 2).

Throughout the entire study period, the principal component remained Dihydro-3-methylene-5-methyl-2-…, with its content ranging from 23.82% to 32.43%. Following its maximum level in 2021 (32.43%), a decrease was observed in 2022, followed by a gradual recovery and increase by 2025 (30.39%), indicating a temporary redistribution of metabolic fluxes with subsequent stabilization.

The second most abundant compound, 5-hydroxymethylfurfural, exhibited a relatively narrow fluctuation range (13.93–17.60%) without pronounced peaks. However, a slight decrease in its content was observed by 2025, which may suggest a reduction in the intensity of carbohydrate degradation processes or alterations in the conditions of its formation.

The sugar alcohol fraction, represented by sorbitol, showed pronounced dynamics: a sharp increase in 2022 (14.59%) was followed by stabilization at 11.99–13.56% during 2023–2025. This trend may reflect adaptive changes in carbohydrate metabolism. In contrast, the content of d-mannitol, 1,4-anhydro- varied within a narrower range (5.17–8.08%) and did not exhibit a clear directional trend.

The group of fatty acids and their derivatives (including 9,12-octadecadienoic acid and 9,12,15-octadecatrienoic acid) remained relatively stable, with only minor fluctuations, indicating the conservative nature of the lipid profile. A similar pattern was observed for organic acids (such as sorbic acid and oleic acid) and other minor components, whose contents remained within the range of 1.5–2.5%.

Overall, the observed dynamics indicate that the phytochemical composition of *Sorbus aucuparia* L. maintains qualitative stability with moderate quantitative variations. The most pronounced shifts are observed in specific metabolic groups—primarily carbohydrate-derived compounds—during the initial period (2021–2022), after which the system transitions to a state of relative equilibrium with only minor fluctuations in the concentrations of individual constituents.

3.3. Seasonal dynamics of phytochemical composition (summer vs. autumn)

The dumbbell chart illustrates a comparative analysis of ten dominant phytochemical compounds in the fruits of *Sorbus aucuparia* (rowan) during the summer and autumn vegetation periods (Figure 3; Supplementary Material Table 1A, Table 2B, Table 3B).

The most pronounced seasonal variation is observed for dihydro-3-methylene-5-methyl-2-furanone: the content of this lactone decreases markedly from 30.4% in summer to 10.6% in autumn, indicating its intensive metabolism during fruit maturation.

An opposite trend is characteristic of sugar alcohols: the concentration of sorbitol increases from 7.0% to 21.7%, while that of 1,4-anhydro-D-galactitol rises from 4.7% to 18.6%. This phenomenon may be explained by the activation of the polyol pathway of carbohydrate metabolism as the plant prepares for the winter period.

The content of 5-hydroxymethylfurfural decreases from 13.9% to 3.7%, suggesting a reduction in sugar thermal degradation processes.

In contrast, the level of *n*-hexadecanoic acid increases from 1.3% to 11.0%, reflecting the accumulation of saturated fatty acids, likely associated with the cryoprotective stabilization of cellular membranes.

The sunburst chart represents the hierarchical structure of the phytochemical composition with clear seasonal differentiation (Figure 4). The inner ring divides the dataset into two vegetation periods (summer and autumn), while the outer ring displays the proportional contribution of each phytochemical class. During the summer period, three major classes dominate: lactones (30.9%), sugar alcohols (26.2%), and furans (15.23%), which together account for 72.3% of the total content of identified compounds. In contrast, the autumn profile is characterized by pronounced monodominance of sugar alcohols (52.16%), visually represented by an expanded segment in the chart. Fatty acids constitute the second most abundant class in autumn (21.17%). The gradient color scale (from yellow to red) encodes relative concentration, enabling clear identification of compositional maxima. Overall, the visualization demonstrates a fundamental metabolic reorganization: a shift from the predominance of secondary metabolites (lactones and furans) toward the accumulation of primary metabolites (sugar alcohols and fatty acids), which are associated with energy storage and osmoprotective functions.

4. Discussion

The investigation of the phytochemical profile of *Sorbus aucuparia* L. fruits using gas chromatography–mass spectrometry (GC–MS) provided a detailed insight into the dynamics of biologically active compound accumulation, substantially complementing existing literature data.

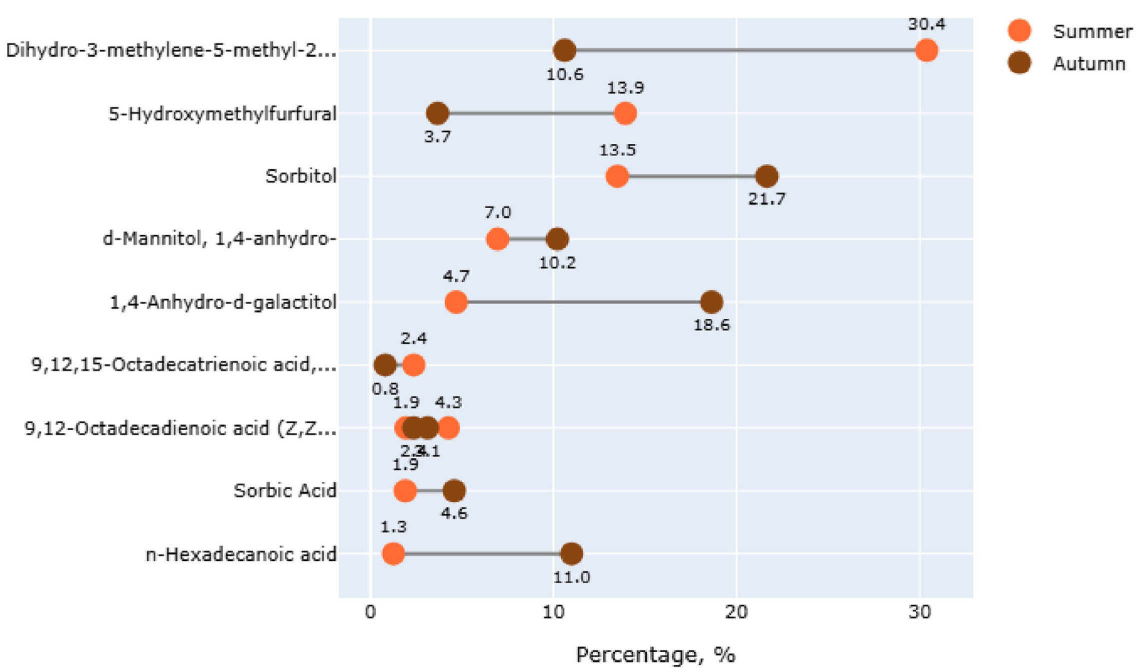

Figure 3. Top 10 compounds of rowan (Summer vs Autumn).

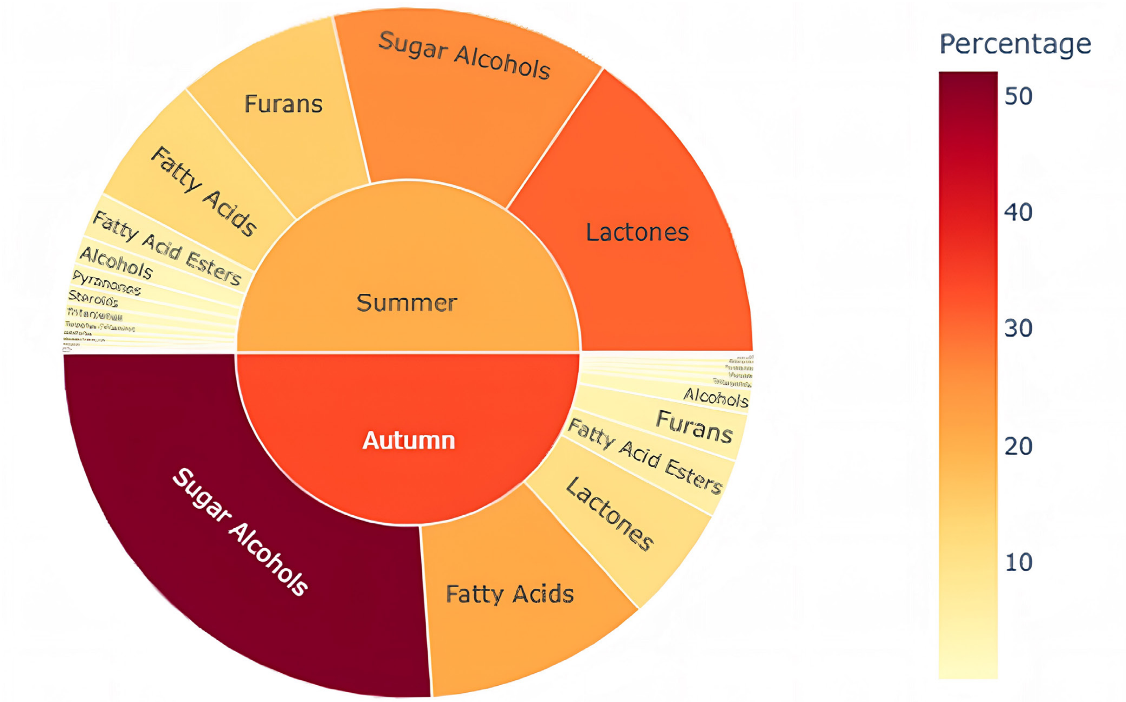

Figure 4. Hierarchical distribution of compound classes in rowan (Summer vs Autumn).

According to the results of Zymone et al. (2018), obtained using high-performance liquid chromatography (HPLC), rowan fruits are a rich source of hydrophilic compounds; however, the application of GC–MS in the present study enabled the identification of a broad spectrum of lipophilic and volatile constituents that are often overlooked in liquid chromatography analyses. Our findings reveal a complex metabolic adaptation of the plant during the transition from summer to autumn, supporting the concept of high plasticity of the chemical composition of *Sorbus* depending on the vegetation period.

Sugars and sugar alcohols represent a key fraction of the extract analyzed by GC–MS. In both examined samples, sorbitol was the dominant component, with a content of 13.49% in the summer period, increasing to 21.66% in the autumn sample. This observation is fully consistent with the findings of Zymone et al. (2018), who also identified sorbitol as the predominant component of the sugar profile in most cultivars studied by HPLC. The status of rowan as one of the richest natural sources of sorbitol has also been confirmed by other authors (Kylli et al., 2010). Such a high concentration of this sugar alcohol is of considerable therapeutic relevance. As noted by Chukwuma and Islam (2017), sorbitol contributes to effective glycemic control by inhibiting intestinal glucose absorption, suggesting that the extracts obtained in this study may be promising ingredients for functional diabetic nutrition.

In parallel with sugar accumulation, GC–MS analysis revealed high activity of carbohydrate metabolism, reflected in the presence of furan derivatives. The elevated content of 5-hydroxymethylfurfural (up to 13.93%) and dihydro-3-methylene-5-methyl-2-furanone (30.39% in the summer sample) indicates intensive chemical transformations occurring in ripening fruits. Within the overall phytochemical profile, these furanones may serve as specific markers of biological activity, in agreement with Raudonis et al. (2014), who emphasized the importance of comprehensive profiling for authentication of *Sorbus*-derived products.

An important aspect of this study was the confirmation of sorbic acid presence using GC–MS, with its content increasing from 1.91% to 4.58% by autumn. This finding supports the conclusions of Brunner (1985) and De Jesus et al. (2021), suggesting that rowan fruits function as a unique natural bioreactor for the synthesis of this natural preservative. Sorbic acid, due to its pronounced antifungal properties, in combination with phenolic compounds described by Zymone et al. (2018), contributes to the strong protective and preservative effect of the extract.

The lipophilic fraction identified by GC–MS revealed important constituents often missed in conventional analyses (Raudonė et al., 2015). The fatty acid profile demonstrated a significant seasonal increase in *n*-hexadecanoic acid (palmitic acid), from 1.26% to 10.99%. Together with unsaturated fatty acids such as oleic acid and 9,12-octadecadienoic acid, these compounds play a crucial role in maintaining and restoring the integrity of the epidermal barrier. The marked increase in fatty acid content in autumn may serve as an indicator of fruit maturation, which is critical for preserving nutritional value (Fiedor and Burda, 2014).

Within the lipophilic fraction, mass spectrometry also enabled the identification of triterpenoids and vitamins, including α-amyrin, β-amyrin, vitamin E, and squalene.

The presence of these compounds explains the pronounced regenerative and antioxidant properties of the extract, as reported by Sarv et al. (2020) and Šavikin et al. (2017). Squalene, being a natural component of human sebum, significantly enhances the bioavailability of cosmetic formulations based on *S. aucuparia*. The presence of tocopherol (vitamin E) in the autumn sample (0.94%) further confirms the high antioxidant potential of the raw material, in agreement with the conclusions of Zymone et al. (2018) regarding the importance of preserving the vitamin complex.

The high antimicrobial activity of the extract against pathogens such as *Staphylococcus aureus* and *Propionibacterium acnes* can be attributed to the synergistic interaction of compounds identified by GC–MS. In addition to phenolic acids, hydroquinone and 2-methoxy-4-vinylphenol were detected, both exhibiting direct antiseptic activity. Of particular interest is the observed synergism of the extract with erythromycin. This effect is likely associated with the presence of phytosterols such as β-sitosterol and campesterol. As reported in the literature (Mikulic-Petkovsek et al., 2017), these compounds are capable of modifying bacterial membranes, thereby increasing their permeability to antibiotics.

In conclusion, the application of GC–MS enabled a deeper understanding of the chemical composition of rowan fruits compared to classical analytical approaches. The results highlight the importance of harvesting fruits at full maturity to obtain extracts with maximal concentrations of sorbitol, sorbic acid, and phytosterols. Overall, the findings confirm the high potential of *Sorbus aucuparia* L. as a valuable raw material for pharmaceutical applications.

5. Conclusion

This study evaluates the seasonal and interannual dynamics of the phytochemical composition of Sorbus aucuparia L. fruits using GC–MS. The results show that the phytochemical profile is characterized by overall qualitative stability combined with moderate quantitative variability, reflecting adaptive metabolic processes.

During 2021–2025, a stable dominance of key compounds was observed, particularly Dihydro-3-methylene-5-methyl-2-..., with minor fluctuations and recovery trends. 5-hydroxymethylfurfural remained relatively stable, indicating controlled carbohydrate transformations. In contrast, sorbitol exhibited the most pronounced variability, suggesting adaptive shifts in carbohydrate metabolism, while lipid and organic acid fractions remained largely conserved.

Seasonal analysis revealed that autumn samples (full maturity stage) are enriched in major bioactive compounds, including sorbitol, sorbic acid, and fatty acids, whereas earlier stages showed higher variability and increased levels of intermediate metabolites such as furan derivatives.

The use of GC–MS enabled the identification of a broader spectrum of volatile and lipophilic compounds, including tocopherols, squalene, and phytosterols, contributing to the antioxidant and antimicrobial potential of the extracts.

Overall, the findings confirm that *Sorbus aucuparia* L. maintains a stable core phytochemical profile with adaptive quantitative shifts influenced by seasonal and interannual factors. The highest accumulation of bioactive compounds occurs at full ripeness, highlighting its potential for pharmaceutical, nutraceutical, and cosmetic applications and the importance of optimal harvest timing.

Data Availability Statement

All the data that support the findings of this study are available in the main text.

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Supplementary Material

Supplementary material accompanies this paper.
Table 1A. Results of chromatographic analysis of rowan extract (2021–2025)
Table 2B. Results of chromatographic analysis of rowan extract (summer, 2025)
Table 3B. Results of chromatographic analysis of rowan extract (autumn, 2025)
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