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OXIDATION OF POLYPRENOLS IN VITIS VINIFERA L. LEAVES

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Abstract

The study presents data on the oxidation reaction of polyprenols (PP) in grape leaves (*Vitis vinifera* L.) containing isoprene units with $n = 10–12$ in the following ratio: $n = 10$ (8.3%), $n = 11$ (42.4%), and $n = 12$ (49.3%). The oxidation process was carried out under conventional conditions using a solvent and under microwave irradiation (MWI) in the absence of a solvent. The influence of MWI on the oxidation efficiency and selectivity of the process was analyzed. The obtained results demonstrate the potential of MWI as an effective and environmentally friendly method for the oxidation of polyprenols in grape leaves.

Keywords: *Vitis vinifera L., leaves, polyprenols, oxidation, microwave irradiation, isoprene units, solvent-free, selective oxidation, environmentally friendly, reaction efficiency, green chemistry, oxidative process, molecular transformation, natural compounds, alternative methods, bioactive substances, structural modification, sustainable synthesis*

Introduction

It is known that polyprenols in plants occur as polyprenyl homologs (Kukina T.P., Bayandina I.I., Pokrovsky A.N., 2007). Unlike most plants, the polyprenols in *Vitis vinifera* L. leaves contain a lower number of polyprenyl homologs (3–4), with the content of prenols with $n = 13$ being minimal. Column chromatography primarily isolates polyprenol fractions with $n = 10–12$, yielding more than 2.0% of the air-dried mass, making them suitable for modification. Additionally, Uzbekistan has sufficient raw material reserves of *Vitis vinifera* L. (Temurov Shukur. 2005). Therefore, studying the modification of grape leaf polyprenols is of great interest.

The chemical transformations of polyprenols are of interest due to their biological role in living organisms. Polyprenols are natural low-molecular-weight bioregulators that facilitate the transport of hydrophilic particles across cell membranes during the biosynthesis of polysaccharides, glycoproteins, and other carbohydrate-containing polymers (Lamani, E. et. al. 2006). The presence of an isoprenoid substituent in some aromatic molecules enhances their biological activity (Chukicheva I.Yu., Fedorova I. V., Koroleva A. A., Kuchin A. V., 2018).

Plant-derived polyprenols, as promising synthons for pharmaceutical development, improve interactions with cell membranes, allowing for the design of targeted drugs (Koroleva A. A., Karmanova L. P., Belykh D. V., Kuchin A. V., 2006). The chemical properties of polyprenols must be considered when studying their transformations. As partially saturated alkyl terpenoid alcohols ($R_2C=CH-CH_2-X$, where X is a functional group), polyprenols have C–X bond dissociation energies 50–105 kJ/mol lower than their saturated analogs, making them highly chemically reactive.

For modification, we used polyprenols from *Vitis vinifera* L. leaves cultivated in the Surkhandarya region, containing isoprene units with $n = 10–12$ and a purity of 95–97% based on HPLC data, in the following ratios: $n = 10$ (8.3%), $n = 11$ (42.4%), $n = 12$ (49.3%) (Zokirova U. T., Khidyrova N. K., Khodjaniyazov H. U., Shakhidoyatov Kh. M., 2013).

Microwave irradiation (MWI) has been used to accelerate chemical reactions since 1986 (Gedye R., Smith F., Westaway K., Ali H., Baldisera L., Laberge L., & Rousell, J., 1986; Berdonosov S. S., 2001). Over time, its application in organic synthesis has expanded significantly (Berdonosov S. S., Berdonosova D. G., Znamenskaya I. V. 2000; Romanova N. N., Kudan P. V., Gravis A. G., Bundel Yu. G., 2000). Therefore, in this study, oxidation reactions of grape leaf polyprenols were conducted under conventional conditions with a solvent and under MWI without a solvent to compare their efficiency and selectivity.

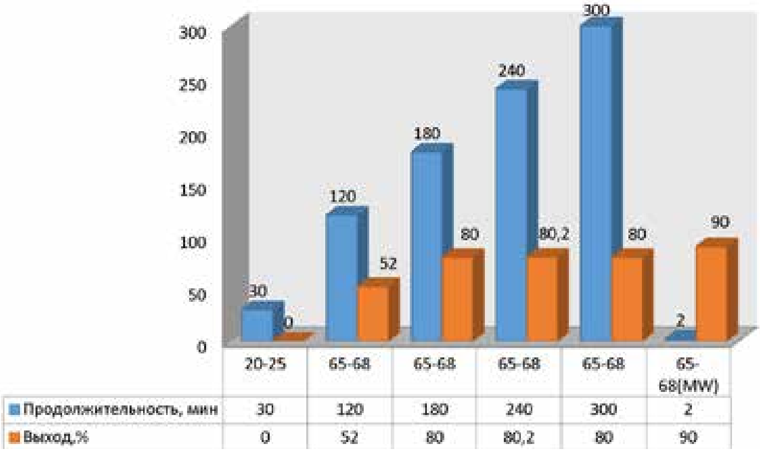
Materials and Methods

Polyprenols (1) were extracted from the leaves of *Vitis vinifera* L. growing in the Surkhandarya region using a previously described method (Zokirova U. T., Khidyrova N. K., Khodjaniyazov H. U., Shakhidoyatov Kh. M., 2013).

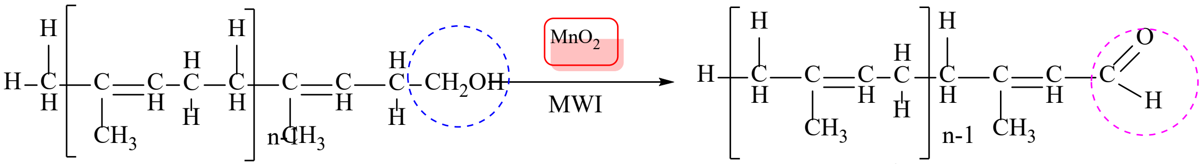
Determination of the Homologous Composition of Polyprenols. The fraction analysis was performed using an Agilent Technologies-1100 chromatograph on a 0.46 × × 150 mm Eclipse XDB-C-18 column. The elution phase was gradient: 0–20 min 0–75% B; 20–25 min 75–100% B; 25–30 min 100–0% B, with a flow rate of 0.75 mL/min, and total analysis time of 30 min. System A – a mixture of methanol-water 9:1 (v/v), B – methanol-hexane-isopropanol 2:1:1. The chromatographic profile was recorded at 210 nm. The quantity of prenols was determined relative to the chromatogram of a standard sample by comparing peak areas using Agilent Chemstation software. Polyprenols from *Rhus coraria* leaves were used as the standard reference.

Oxidation of Polyprenols was carried out using a freshly prepared solution of manganese dioxide in hexane, resulting in the formation of a nucleophilic reaction center at the carbonyl carbon. The reaction was initially conducted at room temperature with stirring for 0.5 hours, but no oxidation occurred. The reaction was then performed under reflux, with the reaction progress monitored hourly using TLC. The obtained data are presented in Figure 1. As a result of the reaction, polyprenal (2) was formed.

Figure 1. *Effect of Time on the Progress of Polyprenol Oxidation*



Maximum yield of polyprenal under normal conditions was 80.0%. Increasing the duration to 5 hours did not yield positive results. To accelerate the oxidation process and increase the product yield, the reaction was conducted under microwave irradiation conditions. Polyprenol oxidation under microwave irradiation occurs within 2 minutes, increasing the polyprenal yield to 90%. Thus, the use of microwave irradiation accelerates the oxidation process by 180 times and increases the polyprenal yield by 9% (Scheme 1):

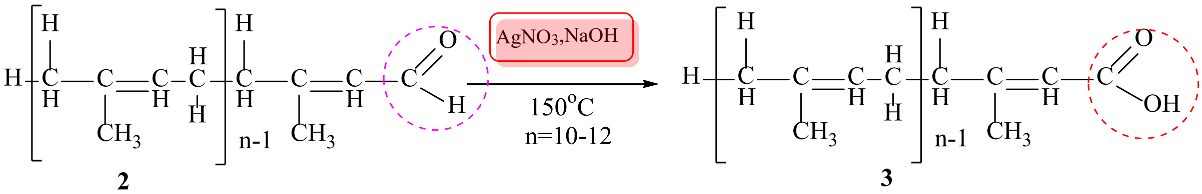


Scheme 1. Polyprenol Oxidation Reaction

The structure of polyprenal (2) was confirmed using spectral analysis methods. The appearance of an absorption band at 1643 cm⁻¹ in the IR spectrum, corresponding to the stretching vibrations of the C=O bond in the aldehyde group, and the disappearance of the hydroxyl group absorption band at 3300 cm⁻¹ confirm the formation of polyprenal aldehyde.

In the ^1H NMR spectrum, signals at 1.63, 1.70, 1.98 ppm (s, CH_3), 2.05 ppm (m, CH_2), a broad signal at 5.14 ppm (s, C=CH), 6.04 ppm (s, H-2), and 9.80 ppm (s, CHO) further confirm the formation of polyprenal.

For the synthesis of polyprenyl acid (3), polyprenyl aldehyde (PPA) was oxidized using silver oxide (molar ratio PPA: $AgNO_3$ = =1:2, 1:3, and 1:4). The reaction was conducted by heating at 150 °C for 1 hour, yielding polyprenyl acid at 50–52% (Scheme 2):



Scheme 2. Synthesis of Polyprenyl Acid

The appearance of an absorption band at 1665 cm⁻¹ in the IR spectrum, corresponding to the stretching vibrations of the C=O bond, and a band at 3327 cm⁻¹ for the hydroxyl group confirm the formation of polyprenyl acid (PPA).

Experimental Part

Synthesis of Polyprenal under Normal Conditions (2). Polyprenol 1 (0.40 g, 0.522 mmol) was dissolved in 10 mL of hexane, and 1.2 g of active manganese dioxide (MnO_2) was added. The reaction mixture was stirred on a magnetic stirrer for 3 hours at a temperature of 75–78 °C, then cooled to room temperature, filtered, and the precipitate was washed three times with hexane and dried over anhydrous sodium sulfate. The solvent was then removed using a rotary evaporator. PPA was purified on a 60 × 1.8 cm silica gel column (100/160 mesh). A mobile phase of hexane/diethyl ether in the ratios 100:1, 100:2, and 100:5 was used. For TLC, the systems hexane/diethyl ether = 3/1 (Rf = 0.65) and benzene–EtOAc 24:1 (R_f = 0.67) were used. Polyprenal 2 was obtained as a light yellow oil (0.32 g, 80% yield).

Synthesis of Polyprenal (2) under Microwave Irradiation (MWI). To a solution of polyprenol 1 (0.10 g) in 1 ml of hexane, 0.25 g of active MnO_2 was added. The mixture was stirred for 2 minutes at 450 W in MWI. Further processing was carried out according to the general procedure. As a result, 0.089 g of yellow oil was obtained, with a polyprenal yield of 89%.

IR Spectrum of Polyprenal (KBr, vmax, cm⁻¹): 2738–3040, 1680 (C=O), 1633, 1450, 1390, 1100, 1041, 853.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.63, 1.70, 1.98 (s, CH_3), 2.05 (m, CH_2), 5.14 (br s, C=CH), 6.04 (s, H-2), and 9.80 (s, CHO).

Synthesis of Polyprenyl Acid (3). To a solution of polyprenyl aldehyde (PPA) (0.25 g, 0.326 mmol) in 2.5 mL of methanol, 0.12 g of silver nitrate (0.706 mmol) in 1 ml of water and 0.1 g of sodium hydroxide dissolved in 2 mL of water were added at molar ratios PPA: $AgNO_3$ = 1:2, 1:3, and 1:4. The reaction was conducted at 150 °C for 1 hour. The yield of polyprenyl acid was 0.123 g (50%). R_f = = 0.52 (PE-DE 3:1 system). **IR Spectrum of Polyprenyl Acid** (KBr, ν_{max}, cm⁻¹): 3327–3600 (broad, OH), 1665 (C=O), 1448, 1376, 1086, 999, 837.

Conclusion

Thus, the study of the oxidation reaction of polyprenols (PP) from grape leaves (*Vitis vinifera* L.) under conventional conditions using a solvent and under microwave irradiation (MWI) without a solvent demonstrated that oxidation under MWI significantly accelerates the process by 180 times and increases the yield of polyprenal by 9%. This method provides a more efficient and rapid approach to obtaining polyprenal, making it a promising alternative for industrial and laboratory applications. The use of MWI enhances reaction efficiency, reducing processing time and improving overall yield.

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