PHENOLIC ACIDS FROM THE INDUSTRIAL WASTES OF *Pelargonium roseum*

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We are studying the chemical composition of industrial wastes of *Pelargonium roseum* Wild (rose pelargonium) formed in the process of obtaining its essential oil.

The wastes (5 liters) were concentrated on the water bath to 1/5 of their initial volume. Two-dimensional chromatography in systems 1) BAW (4:1:2) and 2) 15% CH_3COOH with the use of color reactions showed the presence of five substances [1]. The individual substances were isolated by chromatography on a column (18 × 2 cm) of polyamide. Elution was performed with water and with ethanol in increasing concentrations of from 5 to 30%. The fractions were monitored by paper chromatography in the 2% CH_3COOH system. The ethanolic fractions containing substances (I) and (II) were combined and concentrated in vacuum. Their chromatographic behavior and the results of standard reactions [2–4] showed that compounds (I) and (II) were of acidic nature. Substance (I) was extracted by ethyl acetate from the acidified (to pH 3) ethanolic eluates. The extracts were concentrated in vacuum and chromatographed on a column of polyamide with water until uncolored eluates appeared, and then with 70% ethanol. The ethanolic fractions were concentrated, acidified to pH 3, and extracted with diethyl ether. The concentrated extract was dissolved in water and, after 48 h, substance (I) separated out in the form of pale yellow crystals.

Substance (I), $C_{13}H_{12}O_6$, mp 195–198°C, R_f 0.82 (BAW, 4:1:2); 0.64 [n-butyl acetate–CH_3COOH–$2H_2O$ (4:1:2)]. UV spectrum (MeOH; nm): 299, 326; + NaOAc 281, 312; + MeONa 250, 358; + $AlCl_3$ 315, 363. Fusion with caustic potash formed protocatechuic acid. The diacetyl derivative [acetylation with acetic anhydride, and recrystallization from methanol–diethyl ether (2:1)] melted at 197–199°C. On the basis of the facts obtained, substance (I) was identified as 3,4-dihydroxycinnamic acid (caffeic acid).

Substance (II) was isolated by the exhaustive extraction of the acidified ethanolic eluates with diethyl ether. The concentrated ethereal extract deposited substance (II) with the composition $C_{16}H_{18}O_9$, mp 204–206°C, $[\alpha]_D^{20}$ –33° [c 1.0; methanol–water (4:1)]. UV spectrum (MeOH; nm): 240, 325; + NaOAc 328; + MeONa 261, 377; + $AlCl_3$ 242, 363. The pentaacetyl derivative (acetylation with acetic anhydride in the presence of sulfuric acid) had mp 184–187°C, and protocatechuic acid was found in the products of alkaline cleavage. On acid hydrolysis, substance (II) broke down into caffeic and quinic acids. The attachment of the caffeic acid to C_3 of the quinic acid was shown by the absence of lactone formation [5, 6]. Consequently, substance (III) is 3-caffeylquinic acid (chlorogenic acid).

Taking into account the pronounced antimicrobial properties of hydroxycinnamic acids [7, 8], we investigated the action of the cell sap of rose pelargonium on the growth and development of intestinal and spore-forming bacteria and pathogenic cocci. The experiment was performed on 12 test cultures. Sterile meat-peptone agar was used as the nutrient medium. The results showed that the cell sap of rose pelarogonium in dilutions of 1:4,1:8, and 1:20 completely suppresses or retards the growth of cocci and of bacteria of the intestinal and spore-forming groups.

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ESSENTIAL OIL OF THE LEAVES OF *Citrus wilsonii*

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Citrus wilsonii Tan. is a good frost-resistant stock for citrus plants [1, 2]. We have investigated the chemical composition of the essential oil of the leaves of Wilson's citrus from the Batumi Botanical Garden of the Academy of Sciences of the Georgian SSR collected at the end of April, 1981.

The essential oil was obtained by the steam-distillation method. The oil was isolated from the distillate by extraction with n-pentane, the yield of essential oil being 0.43% on the dry weight.

The composition of the essential oil was determined by gas–liquid chromatography on a Varian Aerograph 1860 chromatograph using a flame-ionization detector. The best separation of the essential oil was achieved on a 550 × 0.2 cm column containing 10% of the stationary phase FFAP on Chromosorb G AW-DMCS 80/100 mesh. The carrier gas was helium at the rate of flow of 40 ml/min. The temperature of the column thermostat was programmed from 100 to 230°C.

The main component was isolated by preparative GLC in an 800 × 0.9 cm column filled with Chromosorb W 60/80 mesh. The monoterpene hydrocarbons were isolated on a column containing 30% of FFAP at 120°C with a rate of flow of the carrier gas of 120 ml/min. The components of the high-boiling fraction were isolated on a column containing 30% of Carbowax 20M at 170°C and a rate of flow of helium of 150 ml/min.

The components isolated were identified by comparing their IR spectra with those given in the literature [3]. Minor components were identified by comparing their retention times with the retention times of known pure substances on columns with different polarities [4].

The components were determined quantitatively by the internal-standard and internal-normalization method [4].

The composition of the essential oil of the leaves of Wilson's citrus was as follows (% on the whole oil): α-pinene, 2.1; β-pinene, 5.2; myrcene, 1.2; limonene, 8.4; α-phellandrene, 0.2; ocimene, 4.4; γ-terpinene, 27.1; p-cymene, 10.3; terpinolene, 0.2; citronellal, 4.3; decanal, 0.4; linalool, 2.9; terpinene-4-ol, 0.6; nonanol, 0.4; α-terpineol, 2.3; neral, 7.5; geranial, 0.3; citronellol, 3.2; nerol, 4.8; geranyl acetate, 3.2; geraniol, 1.4; ylangene, 2.5; caryophyllene, 0.3. Camphene Δ^3-carene, sabinene, octanal, and heptanal were detected in the oil in trace amounts.

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