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COMPOUNDS OF THE ESSENTIAL OIL OF *Phellodendron piriforme*

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Phellodendron (Rutaceae), native to northeast Asia, is a small genus comprising several species [1]. It comprises deciduous, medium sized trees with corky bark, leathery pinnate leaves, yellowish-green flowers, and small, black, aromatic fruits [2, 3]. The most important species of the genus are *P. amurense* Rupr. and *P. chinense* C. K. Schneid. Their bark, containing protaberberine alkaloids, has anti-inflammatory, antipyretic, antidiarrhetic, antibacterial, and antifungal properties. It is commonly used in traditional Chinese medicine and the cosmetic industry [4, 5]. Essential oils of *P. amurense, P. chinense*, and *P. sachalinense* have been the subject of limited previous study [6–12]. *Phellodendron piriforme* E. Wolf (pearfruit cork tree) is a rare species. It grows among others in the Arnold Arboretum of Harvard University, Dickinson Research Center, North Dakota State University, and the Botanical Garden of the Academy Sciences of Tashkent [13]. There is only one report on the bioactive substances in this species. Flavonol glycoside phellavin was found in leaves [13].

The aim of the present research was to determine the chemical composition of the essential oils from fruits, flowers, and leaves of *P. piriforme*. The components of the oils are given in Table 1, including their percentages and retention indices (RI). The constituents are listed in order of their elution from a CP Sil 5CB column. About 90 components, representing 98–99% of the oils, were identified. The fruit oil contained mainly monoterpene hydrocarbons (70%) and sesquiterpene hydrocarbons (22%). Myrcene (66.7%) was the principal constituent of the oil, followed by germacrene D (14.1%) and β-caryophyllene (3.4%). The flower and leaf oils contained mono- and sesquiterpene hydrocarbons as well as oxygenated sesquiterpenes. The main constituents of the flower oil were myrcene (23.8%), limonene and β-phellandrene (9.7%), germacrene D (7.2%), (*Z*)-β-ocimene (6.9%), β-elemol (6.6%), and (*E*)-β-ocimene (5.1%). The main constituents of the leaf oil were β-elemol (19.2%), myrcene (12.4%), (*Z*)-β-ocimene (8.7%), limonene and β-phellandrene (7.2%), (*E*)-β-ocimene (6.1%), phytol (4.9%), and germacrene D (4.7%).

The plant material was collected in the Forest Experimental Station, Arboretum of Warsaw Agriculture University in Rogow (Poland), flowers and leaves in June, and ripe fruits in September 2009. Voucher specimens (No. 8–10/2009) were deposited at the Institute of General Food Chemistry, Technical University of Lodz.

The fresh flowers (100 g), fresh leaves (100 g), and fresh crushed ripe fruits (100 g) were separately hydrodistilled for 3 hours using a Clevenger-type apparatus. The essential oils were obtained in yields of 0.05% (v/w) from flowers, 0.01% (v/w) from leaves, and 1.40% (v/w) from fruits. The oils had a pale, yellow color and an intensive terpenic aroma. After decanting and drying over anhydrous magnesium sulfate, they were stored at low temperature before analysis.

The oils were analyzed by GC and GC-MS. GC analysis was performed on a Carlo Erba, MEGA 5300 gas chromatograph equipped with a split-splitless injector and a flame ionization detector using capillary columns: nonpolar CP Sil 5 CB (Chrompack) 30 m, 0.32 mm, film thickness 0.25 μm, temperature program 50–300°C at 4°C/min, injector temperature 320°C, detector temperature 310°C; polar HP Innowax (Agilent J&W) 30 m, 0.25 mm, film thickness 0.25 μm, temperature program 50–245°C at 4°C/min, injector temperature 250°C, detector temperature 260°C; carrier gas helium with flow rate 1 mL/min; volume injected 0.08 μL; split ratio 1:10. GC-MS analysis was performed on a GC 8000 equipped with a mass Fisons MP 800. The MS operating parameters were: ionization voltage 70 eV; ion source temperature 200°C; mass range 33–420 amu. Other conditions of the analysis were the same as described under GC analysis.

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TABLE 1. Composition of the Essential Oils from Fruits, Flowers, and Leaves of *Phellodendron piriforme*

Compound	RI[a]	Fruit	Flower	Leaf	Compound	RI[a]	Fruit	Flower	Leaf
		oil					oil		
Tricyclene	904	0.1	Tr.	Tr.	Germacrene D	1461	14.1	7.2	4.7
α-Pinene	925	0.4	2.5	3.9	Tridecan-2-one	1466	0.1	0.8	0.1
Camphene	938	Tr.	Tr.	Tr.	*epi*-Cubebol	1471	Tr.	Tr.	Tr.
Sabinene	960	Tr.	0.1	0.1	Bicyclogermacrene	1477	0.7	0.7	0.6
β-Pinene	964	0.1	0.1	0.1	α-Muurolene	1480	0.1	0.6	0.4
Myrcene	978	66.7	23.8	12.4	(*E*,*E*)-α-Farnesene	1483	0.1	0.4	0.9
α-Phellandrene	993	Tr.	1.9	1.6	γ-Cadinene	1498	0.1	0.3	0.5
α-Terpinene	1001	Tr.	0.1	Tr.	Cubebol	1500	Tr.	Tr.	Tr.
p-Cymene	1009	Tr.	0.1	0.1	*cis*-Calamenene	1502	–	–	Tr.
Limonene	1016	0.7[b]	9.7	7.2	δ-Cadinene	1504	0.6	0.9	1.4
β-Phellandrene	1016	1.6[b]			Cadina-1,4-diene	1518	Tr.	Tr.	Tr.
(*Z*)-β-Ocimene	1023	0.2	6.9	8.7	α-Cadinene	1522	Tr.	0.1	0.1
(*E*)-β-Ocimene	1033	0.1	5.1	6.1	β-Elemol	1528	0.5	6.6	19.2
γ-Terpinene	1050	Tr.	0.2	0.1	Germacrene B	1538	0.1	Tr.	Tr.
Terpinolene	1057	Tr.	Tr.	Tr.	(*E*)-Nerolidol	1543	0.2	1.3	4.1
Nonan-2-one	1069	Tr.	0.4	0.7	Germacrene D-4-ol	1553	3.0	3.5	4.1
Linalool	1080	0.2	0.7	0.5	Caryophyllene oxide	1565	0.1	Tr.	0.1
Perillene	1085	–	0.1	0.8	Globulol	1578	Tr.	0.1	0.2
allo-Ocimene	1114	Tr.	2.6	3.5	1,10-di-*epi*-Cubenol	1587	0.1	0.1	0.1
Terpinen-4-ol	1139	Tr.	Tr.	0.2	1-*epi*-Cubenol	1607	0.1	0.1	0.2
α-Terpineol	1158	Tr.	Tr.	Tr.	γ-Eudesmol	1616	–	0.8	0.9
Citronellol	1218	Tr.	Tr.	Tr.	*epi*-α-Cadinol	1618	Tr.	Tr.	Tr.
Nerol	1222	Tr.	Tr.	Tr.	*epi*-α-Muurolol	1621	0.1	0.3	0.3
Geraniol	1252	Tr.	1.1	3.2	Cubenol	1623	0.1	0.4	0.1
Linalyl acetate	1255	Tr.	0.3	0.1	β-Eudesmol	1625	–	0.1	0.1
Methyl citronellate	1269	0.1	Tr.	Tr.	α-Cadinol	1628	0.5	2.0	1.4
Methyl nerolate	1276	–	–	Tr.	α-Eudesmol	1643	–	0.8	0.6
Undecan-2-one	1290	0.4	0.3	–	(*Z*,*Z*)-Farnesol	1676	0.1	Tr.	Tr.
Undecan-2-ol	1314	Tr.	0.3	–	(*E*,*E*)-Farnesol	1688	1.6	2.5	0.3
Methyl geranate	1319	Tr.	0.3	Tr.	(2*Z*,6*E*)-Farnesol	1706	Tr.	Tr.	Tr.
Bicycloelemene	1323	Tr.[b]	0.7	0.4	(*E*,*E*)-Farnesyl acetate	1828	0.1	0.1	0.1
δ-Elemene	1323	1.0[b]			Nonadecane	1903	–	0.1	0.2
α-Terpinyl acetate	1329	0.1	0.1	Tr.	Palmitic acid	1918	–	1.0	0.1
Citronellyl acetate	1332	Tr.	Tr.	Tr.	Phytol	1988	–	–	4.9
α-Cubebene	1337	Tr.	Tr.	Tr.	Eicosane	2002	Tr.	0.1	Tr.
Neryl acetate	1347	Tr.	–	–	Heneicosane	2098	Tr.	0.3	0.1
Geranyl acetate	1350	0.3	0.4	Tr.	Docosane	2196	Tr.	0.3	Tr.
α-Copaene	1362	0.3	0.1	0.1	Tricosane	2291	Tr.	1.8	0.1
β-Bourbonene	1370	Tr.	Tr.	Tr.	Tetracosane	2394	Tr.	0.4	Tr.
β-Cubebene	1377	0.2[b]	0.5	0.4	Pentacosane	2498	Tr.	1.8	0.1
β-Elemene	1377	0.4[b]			Total		99.5	98.8	99.6
(*E*)-β-Damascone	1389	–	–	0.1	Monoterpene hydrocarbons		70	52	44
α-Gurjunene	1397	0.1	Tr.	Tr.	Oxygenated monoterpenes		1	4	4
β-Caryophyllene	1401	3.4	3.7	2.0	Sesquiterpene hydrocarbons		22	17	13
β-Gurjunene	1411	0.2	0.5	0.4	Oxygenated sesquiterpenes		6.5	19	32
trans-α-Bergamotene	1427	0.1	0.1	0.1	Diterpenes		–	–	5
α-Humulene	1434	0.3	0.6	0.5	Aliphatic hydrocarbons		0.5	5	1
(*E*)-β-Farnesene	1438	0.1	0.1	Tr.	Acids		–	–	0.1
γ-Muurolene	1442	0.2	0.2	0.4					

Tr.: trace (<0.05%); [a]data from CP Sil 5 CB column; [b]data from HP Innowax column.

Identification of the components of the oils was based on retention indices (RI) relative to *n*-alkanes and mass spectra (MS) using computer libraries NIST, Wiley, MassFinder, and literature [14]. The percentage composition of the oils was computed from GC peak areas without the use of correction factors.

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