

КОМПОНЕНТНЫЙ СОСТАВ РЕСУРСНЫХ ВИДОВ

PHYTOCHEMICAL FEATURES OF *MALABAILA DASYANTHA* (APIACEAE) AERIAL PARTS

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Malabaila dasyantha (C. Koch) Grossh (Apiaceae) is one of the species widely used in folk medicine. However, scientific research of this species has not been carried out, and almost no information on it is found in academic scientific databases. The new distribution areas of *M. dasyantha* were discovered in Gadabay district, Azerbaijan. It was determined that the plant belongs to the xerophytic ecological group. The chemical composition of the species was studied, focusing on the isolation and elucidation of phytochemical structures. The aerial parts of *Malabaila dasyantha* were finely cut and dried at ambient conditions. The mixture of extractive substances was obtained through three consecutive extractions with acetone, each 3 days long. The resulting acetone was filtered and evaporated on a water bath, resulting in a yellow resin with a 7% yield. The resin was then dissolved in CHCl_3 and chromatographed over a column of neutral Al_2O_3 with elution by hexane, hexane + benzene, benzene, benzene + chloroform, chloroform, and chloroform + ethanol, in different ratios. Each fraction had a volume of 100 mL, and the separation and isolation process was carried out using column (silica gel) and thin-layer chromatographic methods. The structural elucidation of the purified compounds was based on infrared spectroscopy, ultraviolet, ^1H and ^{13}C -NMR data, and compared with those previously reported in the literature. The isolated compounds from the acetone extracts of *M. dasyantha* were identified as scopoletin (4.3%), oxypencedanin (2.6%), isoimperatorin (3.5%), and columbianetin (2.5%). These findings may have potential applications in the fields of medicine and pharmacology. Further studies are needed to fully explore the potential of these compounds and their therapeutic properties.

Keywords: *Malabaila dasyantha*, Apiaceae, distribution areas, phytochemicals, bioactive compounds, Azerbaijan

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Apiaceae is a large family, composed of more than 3700 species belonging to 434 genera all around the world [1, 2]. In Azerbaijan, 187 species from 76 genera have been identified. They are distributed in both plains and mountains [3]. One of these genera is *Malabaila* Hoffm., which belongs to the Umbelliferae family and was described in 1814. The Plant List includes 78 scientific plant names of species rank for the genus *Malabaila* [4]. The Umbelliferae (or Apiaceae) family has a cosmopolitan spreading, but most of Apiaceae taxa are confined to northern temperate regions, and high altitudes in the tropical regions [5]. The *Malabaila* genus is represented by 10 species in the Mediterranean region, Central Asia, Iran, and the Caucasus [6]. Chemical constituents found in the

Apiaceae family include volatile oils, coumarins, acet-ylenes and flavonoids, while terpenes, sesquiterpenes and alkaloids are rare [7].

Two species of *Malabaila* (Apiaceae) genus are known to grow in Azerbaijan: *Malabaila dasyantha* (C. Koch) Boiss. (fig. 1) and *Malabaila sulucata* (C. Koch) A. Grossh [6]. These species differ in stem shape and the number of umbel rays [8]. The distribution of phyto-geographic elements is Irano-Turanian (*M. dasyantha*) [8]. *M. dasyantha* is used in folk medicine for nail disorders and to treat hemorrhoids [8–10]. Our findings show that in Azerbaijan this species has a resource potential in a small area of the middle mountain range of Gadabay region, among grasses of rocky areas. The species has a small area of distribution in few biogeographic areas due to its sensitivity to changing environmental conditions (low temperature) and belongs to the xerophytic ecological group. One of the main features of the plant is that it is drought tolerant due to the proper management of water transport: this feature is

List of abbreviations. TLC: Thin layer chromatography; IR: Infrared Spectroscopy; UV: Ultraviolet; NMR: Nuclear Magnetic Resonance; ^1H NMR: Proton nuclear magnetic resonance; DMSO: Dimethyl sulfoxide; ^{13}C NMR: Carbon-13 nuclear magnetic resonance.



Fig. 1. *Malabaila dasyantha* (C. Koch) Grossh flowering phase (June 10) and seed formation phase (July 15).

associated with the cytoplasm properties and distinguishes it from other groups of [11]. We observed that water deficiency causes morphological changes, including smaller leaf blades and poor growth of the plant. Under sufficient water supply, leaves are elastic, and the growth of the plant is fast, indicating that *M. dasyantha* is not an arid but a drought-tolerant xerophytic plant. Over time, due to changes in environmental conditions, the plant can expand or reduce its distribution area. Our investigation further indicates that this plant has a specific areal type, and the species has an appearance and features reflecting its adaptation to ecological conditions.

The study is aimed to determine new distribution areas and chemical composition of *M. dasyantha* species.

MATERIAL AND METHODS

Malabaila dasyantha specimens were collected in Gadabay district of Azerbaijan on July 15, 2021, processed for herbarium, and identified using Herbarium Foundation of the Institute of Botany of the Azerbaijan National Academy of Sciences.

A total of 300 g of dried aerial parts of *M. dasyantha*, which were collected at flowering phase, were subjected to three successive extractions with acetone, each 3 days long, resulting in the procurement of 10 g

of compounds. The column chromatography was employed to obtain separated fractions of compounds. The Al_2O_3 column ($h = 80$; $d = 2.5$ cm) was used for chromatography of the extract. The fractions of 100 mL volume were eluted with hexane (30 fractions), hexane + benzene (40 fractions), benzene (43 fractions), benzene + chloroform (27 fractions), chloroform (10 fractions), and chloroform + ethanol (95 : 5). The thin-layer chromatography (Silifol UV 254, solvent – benzene + chloroform, 1 : 1) was executed to determine the mixture of components. The IR spectra of the substances were recorded using an “Agilent Cary 630 FT, R” spectrophotometer. The chemical structures of the substances were determined by detecting their NMR spectra. The melting temperatures of the obtained substances were determined by utilizing the Boethius table. The substance determination was based on the IR, ^1H , and ^{13}C NMR information on the structure of the individual compounds provided in literature [12].

RESULTS AND DISCUSSION

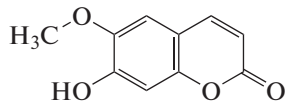
The acetone extraction resulted in the procurement of four individual substances (skopoletin 4.3%, oxypencedanin 2.6%, isoimperatorin 3.5%, and columbianetin 2.5%).

Table 1. Scopoletin infrared (IR) and ultraviolet (UV) spectra and melting temperature

IR-spectrum, ν , cm^{-1}	UV-spectrum, nm (lg ϵ)	Melting point, $^{\circ}\text{C}$
$\nu_{\max}$ 1710 (CO- δ -lactone cycle), 1631, 1613, 1570, 1520 (C=C aromatic cycle)	$\lambda_{\max}$ 229 (4.20), 254 (3.72), 298 (3.77), 346 (4.12)	204.0–205.0

Table 2. ^1H NMR and ^{13}C NMR chemical shift values of scopoletin recorded in CDCl_3

^{13}C NMR		
1–C	C	160
2–C	CH	149.4
3–C	CH	144.4
4–C	CH	111.6
5–C	CH	145
6–C	CH	110.4
7–C	C	102.7
8–C	C	151
9–C	C	109.5
10–C	C	55.94
1. Scopoletin – $\text{C}_{10}\text{H}_8\text{O}_4$		



^1H -NMR (CDCl_3 300 MHz) δ : 10.32 (s, 1H), 7.91 (d, $J = 9.3$ Hz, 1H), 7.22 (s, 1H), 6.78 (s, 1H), 6.23 (d, $J = 9.3$ Hz, 1H), 3.82 (s, 3H).

The chemical shifts (δ values) indicate the relative electron density and shielding of each carbon atom. For example, the carbonyl carbon (C=O) at position 1 has the highest chemical shift at 160 ppm, while the aromatic carbons (C=C) at positions 2–6 have chemical shifts in the range of 110–145 ppm.

The ^1H NMR spectrum provides information about the hydrogen atoms in the molecule and their chemical environment. The spectrum shows six peaks, each corresponding to a different type of hydrogen atom in the molecule. The chemical shifts (δ values) indicate the relative electron density and shielding of each hydrogen atom. For example, the hydrogen atom on the carbonyl group at position 1 appears as a singlet (s) at a chemical shift of 10.32 ppm, while the hydrogen atoms on the aromatic rings appear as singlets or doublets (d) at chemical shifts in the range of 6.23–7.91 ppm.

The scopoletin is an organic compound containing an aromatic ring and a lactone ring, which are confirmed by the ^{13}C NMR spectrum. The ^1H NMR spectrum confirms the presence of hydrogen atoms in the aromatic and lactone rings, as well as a methyl group (CH_3) at a chemical shift of 3.82 ppm (table 2).

Substance – 1 (Scopoletin)

The IR spectrum shows strong absorption bands at $\nu = 1710 \text{ cm}^{-1}$, which are assigned to the CO- δ -lactone cycle. In addition, the IR spectrum also shows characteristic absorption bands at 1631, 1613, 1570, and 1520 cm^{-1} , which can be attributed to the C=C aromatic cycle. The UV spectrum of the compound displays four distinct peaks at $\lambda_{\max}$ 229, 254, 298, and 346 nm with lg ϵ (logarithm of the molar extinction coefficient) values ranging from 3.72 to 4.20. The strongest absorption is observed at $\lambda_{\max}$ 229 nm with lg ϵ 4.20, while the weakest is observed at $\lambda_{\max}$ 298 nm with lg ϵ 3.77. The presence of these absorption peaks in the UV spectrum indicates the presence of conjugated π -electron systems in the compound (Table 1).

The ^{13}C NMR spectrum shows 10 peaks, each corresponding to a different carbon atom in the molecule.

Substance – 2 (Oxypeucedanin)

In the IR spectrum, several characteristic peaks are observed, including a strong peak at 1703 cm^{-1} corresponding to the carbonyl group in a δ -lactone ring, and four peaks in the range of 1554 – 1618 cm^{-1} corresponding to the aromatic C=C bond. These peaks provide information on the functional groups and molecular structure of the compound. In the UV spectrum, four peaks are observed, with maximum absorption occurring at wavelengths of 220, 249, 266, and 306 nm. The lg ϵ values indicate the intensity of absorption at each peak, with higher values indicating greater absorption (Table 3).

In the provided ^{13}C NMR spectrum, we observed the chemical shift of 16 carbon atoms in an unknown molecule. The chemical shift is related to the electron density around each carbon atom, which is influenced

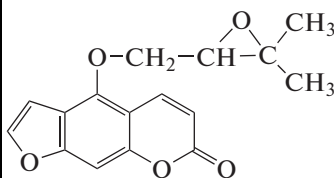
Table 3. Oxypeucedanin infrared (IR) and ultraviolet (UV) spectra and melting temperature

IR-spectrum, ν , cm^{-1}	UV-spectrum, nm (lg ϵ)	Melting point, $^{\circ}\text{C}$
$\nu_{\max}$ 1703 (CO- δ -lactone cycle), 1618, 1603, 1575, 1554 (C=C aromatic cycle)	$\lambda_{\max}$ 220 (4.02), 249 (4.03), 266 (4.02), 306 (3.97)	137.0–138.0

Table 4. ^1H NMR and ^{13}C NMR chemical shift values of oxypeucedanin recorded in CDCl_3

^{13}C NMR		
1-C	C	25.00
2-C	CH	27.00
3-C	CH	30.00
4-C	CH	71.00
5-C	CH	74.00
6-C	CH	94.00
7-C	C	99.00
8-C	C	104.00
9-C	C	108.00
10-C	C	111.50
11-C	C	112.00
12-C	C	119.00
13-C	C	133.00
14-C	C	139.00
15-C	C	145.00
16-C	C	161.00

2. Oxypeucedanin –
 $\text{C}_{16}\text{H}_{16}\text{O}_6$



^1H NMR: 6.30 (d., $J = 9.65$ Hz, 1H, H-3), 8.20 (d., $J = 9.65$ Hz, 1H H-4), 7.30 (s., 1H, H-8), 7.00 (d., $J = 2.30$ Hz, 1H, H-3'), 7.60 m. h. (d., $J = 2.30$ Hz, 1H, H-2')

by the atoms and groups surrounding it. By analyzing the chemical shift values, we can infer the type of carbon atoms and their neighboring functional groups in the molecule.

The ^{13}C NMR spectrum reveals the presence of an aromatic ring system in the molecule. Carbon atoms 1–6 show a distinct pattern of chemical shifts between 25 and 94 ppm, consistent with sp^2 hybridized carbons in an aromatic ring. Additionally, there are 11 aliphatic hydrocarbons present in the molecule showing chemical shifts between 99 and 161 ppm.

The provided ^1H NMR spectrum of oxypeucedanin, a molecule with the molecular formula $\text{C}_{16}\text{H}_{16}\text{O}_6$, further confirms the presence of an aromatic ring system. The proton chemical shifts indicate the presence of five aromatic protons, with chemical shifts at 6.3 ppm (H-3) and 8.2 ppm (H-4) appearing as doublets with a coupling constant of 9.65 Hz, and a singlet at 7.3 ppm (H-8). In addition, the proton chemical shifts at 7.0 ppm (H-3') and 7.6 ppm (H-2') suggest the presence of two meta-coupled aromatic protons (table 4).

Substance – 3 (Isoimperatorin)

The compound has a δ -lactone cycle and an aromatic cycle as evident from its IR spectrum with absorption peaks at 1729 and 1547 cm^{-1} for CO- δ -lactone and 1580 and 1610 cm^{-1} for C=C aromatic cycle.

The UV spectrum of isoimperatorin shows absorption peaks at λ_{max} 222, 250, 259, 268 and 310 nm, indicating the presence of conjugated pi-electron system in the compound (Table 5).

The ^1H NMR spectrum of isoimperatorin shows singlet peaks at 6.30 and 8.15 ppm with a coupling constant of 9.65 Hz and a singlet peak at 7.35 ppm, indicating the presence of aromatic protons. The spectrum also shows doublet peaks at 8.00 and 7.60 ppm with a coupling constant of 2.10 Hz, suggesting the presence of a vicinal pair of protons.

The ^{13}C NMR spectrum of isoimperatorin shows 16 carbon signals with the corresponding chemical shift values, which indicate the presence of various types of carbon atoms, such as CH, C, and CO- δ -lactone carbon atoms.

Overall, the given data suggest that isoimperatorin is a compound with a complex structure that contains an aromatic ring, a δ -lactone cycle, and a conjugated pi-electron system (Table 6).

Substance – 4 (Columbianetin)

The IR spectrum shows absorption bands at 3408 (OH-group), 1716 (CO- δ -lactone), and 1619 and 1580 cm^{-1} (C=C aromatic cycle), indicating the presence of an OH group, a lactone group, and an aromatic ring. The UV spectrum shows absorption peaks at 220 ($\lg \epsilon$ 4.08), 252 ($\lg \epsilon$ 3.52), 262 ($\lg \epsilon$ 3.55), 300 ($\lg \epsilon$ 3.83), and 327 nm ($\lg \epsilon$ 4.18) (Table 7).

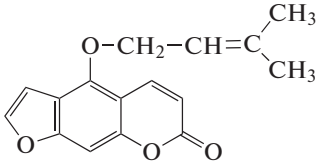
Table 5. Isoimperatorin infrared (IR) and ultraviolet (UV) spectra and melting temperature

IR-spectrum, ν , cm^{-1}	UV-spectrum, nm ($\lg \epsilon$)	Melting point, $^{\circ}\text{C}$
ν_{max} 1729 (CO- δ -lactone cycle), 1625, 1610, 1580, 1547 (C=C aromatic cycle)	λ_{max} 222 (4.38), 250 (4.24), 259 (4.17), 268 (4.17), 310 (4.12)	108.0–109.0

Table 6. ^1H NMR and ^{13}C NMR chemical shift values of isoimperatorin recorded in CDCl_3

^{13}C NMR		
1-C	C	18.6
2-C	CH	26.2
3-C	CH	70.2
4-C	CH	94.7
5-C	CH	105.4
6-C	CH	108.0
7-C	C	113.0
8-C	C	114.7
9-C	C	119.5
10-C	C	139.9
11-C	C	140.2
12-C	C	145.3
13-C	C	149.4
14-C	C	153.1
15-C	C	158.5
16-C	C	161.7

3. Isoimperatorin –
 $\text{C}_{16}\text{H}_{14}\text{O}_4$

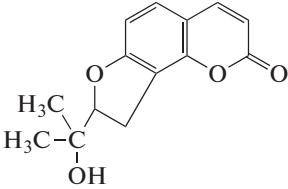


^1H NMR(6.30, 1H, $J = 9.65$ Hz and 8.15 m. h., 1H, $J = 9.65$ Hz), singlet (7.35 m. h., 1H), doublet (8.00, $J = 2.10$ Hz, 1H and 7.60 m. h., $J = 2.10$ Hz, 1H)

Table 8. ^1H NMR and ^{13}C NMR chemical shift values of columbianetin recorded in CDCl_3

^{13}C NMR		
1-C	C	160.2
2-C	CH	151.3
3-C	CH	139.2
4-C	CH	134.3
5-C	CH	132.6
6-C	CH	127.8
7-C	C	125.9
8-C	C	118.8
9-C	C	116.2
10-C	C	72.8
11-C	C	71.0
12-C	C	67.3
13-C	C	66.4
14-C	C	20.8

Columbianetin –
 $\text{C}_{14}\text{H}_{14}\text{O}_4$



^1H NMR (DMSO- d_6 , 400 MHz) δH (ppm) = 6.18 (1H, d, $J = 2$ Hz, H-6), 6.14 (1H, d, $J = 2$ Hz, H-8), 7.53 (1H, d, $J = 8.4$ Hz, H-1'), 6.89 (1H, d, $J = 8.8$ Hz, H-4'), 7.55 (1H, dd, $J = 2.4$ and 8.5 Hz, H-5')

Table 7. Columbianetin infrared (IR) and ultraviolet (UV) spectra and melting temperature

IR-spectrum, ν , cm^{-1}	UV-spectrum, nm (lg ϵ)	Melting point, $^{\circ}\text{C}$
ν_{max} 3408 (OH-group), 1716 (CO- δ -lactone), 1619, 1580 (C=C aromatic cycle)	λ_{max} 220 (4.08), 252 (3.52), 262 (3.55), 300 (3.83), 327 (4.18)	156.0–158.0

The ^1H NMR spectrum of columbianetin, recorded in DMSO- d_6 , shows five peaks. The peak at 6.18 ppm corresponds to a proton on carbon 6 (H-6) and is a doublet with a coupling constant (J) of 2 Hz. The peak at 6.14 ppm corresponds to a proton on carbon 8 (H-8) and is a doublet with a coupling constant of 2 Hz. The peak at 7.53 ppm corresponds to a proton on carbon 1' (H-1') and is a doublet with a coupling constant of 8.4 Hz. The peak at 6.89 ppm corresponds to a proton on carbon 4' (H-4') and is a doublet with a coupling constant of 8.8 Hz. The peak at 7.55 ppm corresponds to a proton on carbon 5' (H-5') and is a doublet of doublets with coupling constants of 2.4 and 8.5 Hz.

The ^{13}C NMR spectrum of columbianetin, recorded in CDCl_3 , shows 14 peaks. The chemical shift values indicate the presence of one carbonyl group (C-2), one lactone group (C-3), and an aromatic ring with six carbons (C-4 to C-9). In addition, there are four methylene carbons (C-10 to C-13) and one methyl carbon (C-14) (Table 8).

CONCLUSIONS

According to the obtained data, in Azerbaijan *Malabaila dasyantha* (C. Koch) Grossh (Apiaceae) has a resource potential in a small area of the middle mountain range of Gadabay region. The study reports the isolation of four novel compounds from the aerial parts of this species. The compounds were identified as scopoletin (4.3%), oxypencedanin (2.6%), isoimperatorin (3.5%), and columbianetin (2.5%), based on rigorous spectroscopic analysis and comparison with their physical properties reported in the literature. Notably, this is the first report of the isolation of these compounds from *M. dasyantha*. The identified coumarin derivatives are expected to have significant medicinal value. Further research is required to explore the potential applications of these novel compounds in the pharmaceutical industry.

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