

STUDIES ON THE ESSENTIAL OILS OF THE PAKISTANI SPECIES OF THE FAMILY UMBELLIFERAE

Part XVI : *Angelica glauca* Edgew ("Chora") seed oil

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Abstract. The essential oil of the seed of *Angelica glauca* of Pakistan, has been studied with respect to its physico-chemical values and chemical composition for the first time. The percentage composition of the oil has been shown as : α -phellandrene (17.70%), terpinyl acetate (30.4%), osthole (19.15%), osthenole (12.63%), angelicin (2.07%) and a mixture of coumarins (13.07%). A marked qualitative and quantitative difference has been noticed in the chemical composition of the essential oil of the local species and that of the similar oils produced elsewhere in the world.

Angelica is a native to Europe and America where it is grown in gardens. In Belgium, France and Germany, it is cultivated for its roots, seeds and stalks, the first two being commercially used for the production of an essential oil to be added to cordials and liqueurs as a flavouring agent.

In Pakistan *Angelica glauca* grows wild in Swat, Gilgit and Azad Kashmir. The plant is recognized as a good cordial and stimulant and the species is useful in flatulence and dyspepsia.

The present studies have been carried out to evaluate the quality and chemical composition of the essential oil of the seed of the species to obtain basic information for the use in developing new agricultural sources of such oils. This communication, therefore, sums up the results of our work on the essential oil of the *Angelica glauca* of Pakistan.

Materials and Methods

Mature seed of the *Angelica glauca* were collected from Muzaffarabad, Azad Kashmir. The essential oil was recovered from the freshly crushed seed by steam distillation. The general methods employed for these studies have been described in the Parts I and II of this series.^{1, 2} A Beckman DB spectrophotometer was used to record ultraviolet spectra of the coumarins. The percentage yield and physico-chemical properties of the essential oil are compiled in Table 1.

The oil (10.g) was split into the hydrocarbon fraction and the oxygenated components by column chromatography using glass column (100 cm \times 3.5 cm) packed with 200 g activated silica gel. The hydrocarbon fraction of the oil was resolved into individual

Results

TABLE 1. PERCENTAGE YIELD AND PHYSICO-CHEMICAL PROPERTIES OF THE ESSENTIAL OIL OF *ANGELICA GLAUCA* SEED.

Constants	Value
Yield	1.3%
Distillation period	15 hr
Colour	Pale
Odour	Sweet; cardamom-like
Specific gravity	0.9800 ²⁴
Refractive index	1.5385 ²⁴
Optical rotation	-3° 10 ²⁵
Acid value	19.45
Ester value	—

components by GLC using nitrogen as carrier gas, flame ionization detector and a 3mm \times 3m copper column, packed with 20% polyethylene glycol succinate (B.D.H. grade) on celite (60-80 mesh) and operated at 140°. The components were identified by coinjecting with authentic samples.

The oxygenated components recovered from the column followed by preparative TLC separation were identified by m.p., uv analysis, TLC and ir comparison with the authentic samples and also by making their known derivatives. The chemical composition of the essential oil thus determined is recorded in Table 2.

Discussion

The hydrocarbon fraction of the oil is mainly constituted of α -phellandrene with a small amount of α -pinene and myrcene.

TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OIL OF *ANGELICA GLAUCA* SEED.

Solvent used	Fraction	Percentage
<i>n</i> -Hexane	Hydrocarbons, mainly α -phellandrene	17.70
20% diethyl ether in <i>n</i> -hexane.	Terpinyl acetate	30.41
8-10% diethyl ether in <i>n</i> -hexane.	Osthole	19.15
15-20% diethyl ether in <i>n</i> -hexane.	Osthole, osthonole	1.35
20-25% diethyl ether in <i>n</i> -hexane	Osthonole	12.63
50% diethyl ether in <i>n</i> -hexane.	Angelicin	2.07
50% ethanol in diethyl ether.	Mixture of coumarins	13.04

In the first oxygenated fraction, terpinyl acetate was identified by TLC and it was also identified by its hydrolysis into α -terpineol and acetic acid. The presence of linallyl acetate in the essential oil of *Angelica glauca* seed had not been reported before.³ It is, therefore, not only a new finding in the essential oil of the local species but the compound also constitutes the major part of the oil.

The next fraction recovered from the column contained osthole, osthonole and angelicin. Osthonole and osthole were identified by m.p., 123° (lit.⁴ 124-25°), 83° (lit.⁴ 82-83°); uv analysis: λ_{EtOH} max. 322, 260 μm , λ_{EtOH} max. 320, 258.5 μm ; ir: (3.0, 3.4, 6.1, 6.8, 7.3, 8.1, 9.3, 11.4, 14.0 μm), (3.4, 5.8, 6.0, 6.2, 6.9, 7.3, 7.6, 8.0, 8.6, 8.9, 9.2, 9.7, 11.6, 12.2, 14.1, 15.1 μm) and TLC comparison with their standard samples. Angelicin was purified by preparative TLC and identified by m.p., 136-137° (lit.⁵ 138-139.5°) and analysis (λ_{EtOH} max. 295, 248 μm). These coumarins have been reported as the constituents of the roots oil but not that of the seed oil of this species. It is quite interesting that we found the existence of an appreciable

amount of the coumarins in the essential oil of the seed of the Pakistani *Angelica glauca*.

The last fraction collected from the column contained a mixture of coumarins and tarry material which have as yet to be identified.

On the basis of the present investigations, it has been concluded that the oil possesses unusual physico-chemical properties and chemical composition. This factor is attributed to climatic conditions. However, the possibility cannot be excluded that the plant may also have developed a new strain and become a different variety.

The oil contains higher percentage of terpinyl acetate, osthole, osthonole and angelicin and relatively large amounts of coumarins. These are the most important and rather characteristic constituents so far as odour and flavour of the oil are concerned. All the above findings suggest that Pakistani *Angelica* seed oil is quite different from and superior to the oils distilled from the European grown species.

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