

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

Part XX. *Pimpinella acuminata* (Edgew) Clarke (Jungli Anise) Seed Oil

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Abstract. The essential oil of the *Pimpinella acuminata* seed with an yield of 0.08% has been investigated with respect to its physico-chemical characteristics and chemical composition. The composition of the oil by GLC has been shown as : pyrrole (1.3%), coniine (4.0%), methyl coniine (70.0%), unknown nitrogenous compounds (4.5%), 1-methyl-2-butyl piperidine (0.9%), 1-methyl-2-pentyl piperidine (3.3%), carvone (0.8%), high boiling hydrocarbons (7.9%), apiole (1.5%), *n*-pentadecane (4.0%), *n*-hexadecane (0.6%), heptadecane (3.0%), unidentified oxy-compounds (2.2%), eugenone (0.4%) and *iso*-pimpinellin (0.6%). The essential oil is chiefly composed of *n*-methyl coniine, one of the alkaloids of *Conium maculatum*,¹ the poison hemlock.

Introduction

Pimpinella acuminata, an umbellifer, is native to Pakistan and India.² It grows wild in the Hazara District, Azad Kashmir and the Murree Hills in Pakistan. The seed of the species is sold in market under the name of *aniso* or *jungli anise*. It is used as a substitute of *Pimpinella anisum* in the local materia medica. On the basis of the constituents of *P. acuminata* as determined in the present work, the seed of the species can find application in painful affections of skin because it possesses an anti-neuralgic and aphrodisiac action.

The present studies have been undertaken because, even though a large quantity of the seed of this plant is brought to the market in Pakistan, yet the content, quality and chemistry of its essential oil are not known. This work, therefore, indicates the results of chromatographic studies on the essential oil of the species for the first time.

Experimental

Materials. Fresh seeds of *P. acuminata* were collected from the Murree Hills. The seeds of the species were also obtained from market at Lahore for comparison purposes.

The essential oil was recovered by dry steam distillation³ of the material. It took 16 hr for complete distillation. The general methods employed for these investigations are described in our earlier publications.³ In addition, a time and temperature programmed GLC, coupled with mass spectrometry, was used to examine the essential oil as such using a glass column (0.25" x 6') packed with 3% Silar 5cp and the various components identified from computerized data.

Results

The physico-chemical values and the chemical composition of the essential oil as worked out from the chromatogram (Fig. 1) are shown in Tables 1-2.

TABLE 1. PHYSICO-CHEMICAL VALUES OF THE ESSENTIAL OIL OF *PIMPINELLA ACUMINATA* SEED

Yield	0.08%
Specific gravity	0.9375 ³⁰
Refractive index	1.4800 ³⁰
Optical rotation	—
Acid value	1.50
Ester value	4.95

The superscripts indicate the temperature at which these parameters were determined.

Discussion

The essential oil of the *P. acuminata* seed, with brown colour and unpleasant smell, was fractionated into hydrocarbons, oxygenated and nitrogenous components by column chromatography.³ The hydrocarbon fraction (11.5%) of the oil, as eluted from the column with *n*-hexane, was mainly composed of high boiling saturated hydrocarbons, viz. *n*-pentadecane, *n*-hexadecane, etc., which were identified by GLC/MS.

The column chromatographic fraction recovered after the elution of hydrocarbons was a mixture of two oxygenated compounds. The fraction was re-chromatographed on silica gel column using 1-5% diethyl ether in *n*-hexane to effect the separation of

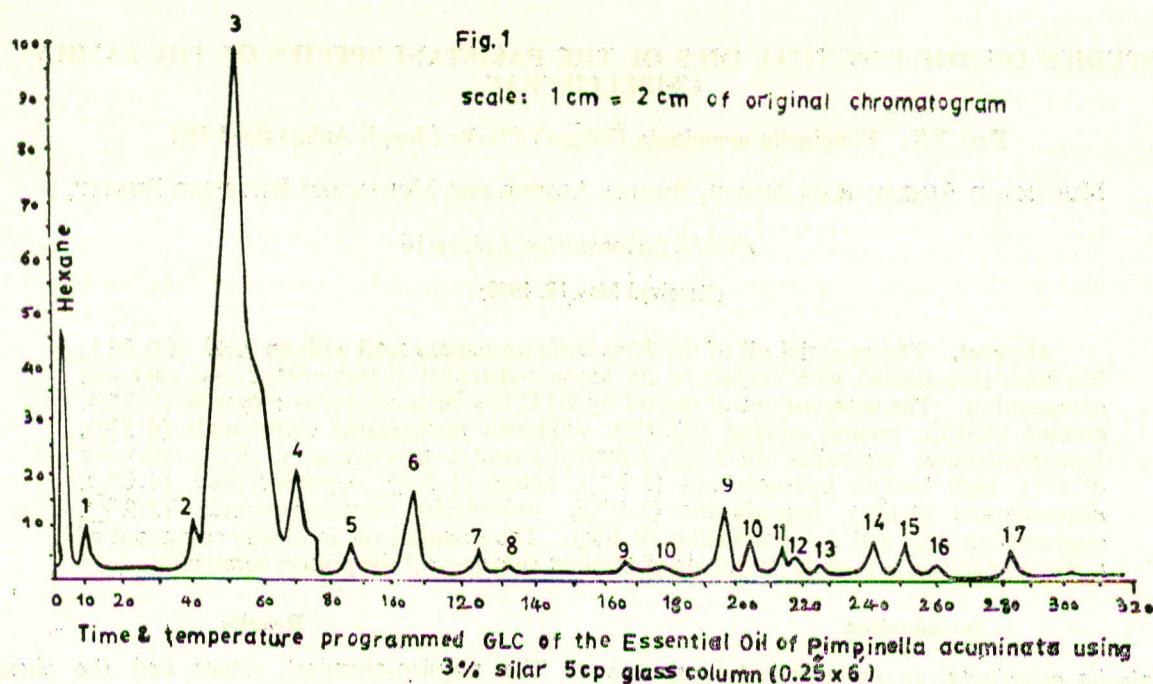


TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OIL OF *PIMPINELLA ACUMINATA* SEED BY GLC.*

Component	Percentage
Pyrrole	1.3
Coniine	4.0
<i>n</i> -Methyl coniine	70.0
Nitrogenous compound (m.w.)	3.9
1-Methyl-2-butyl piperidine	0.9
1-Methyl-2-pentyl piperidine	3.3
Unidentified (m.w. 169)	0.4
Carvone	0.2
<i>n</i> -Pentadecane	4.0
A sesquiterpene	1.7
" "	2.0
Apiole	1.5
<i>n</i> -Hexadecane	0.6
Unknown (m.w. 192)	2.2
" (m.w. 250)	0.4
Heptadecane	3.0
Eugenone	0.6

*This work was carried out by Messrs. R. Kleiman and D. Weisleder for us.

these compounds from each other. The compounds were identified as apiole and carvone by TLC and ir comparison with their standard samples.

After the elution of the oxygenated compounds cited above, a mixture of nitrogenous compounds (eluted with 5-50% diethyl ether in *n*-hexane) was obtained. Their separation into individual components through column chromatography was not successful. However, the major nitrogen containing compounds of the oil was obtained by repeated column chromatography. The ir absorption, S(3.4, 3.5, 3.6, 6.7, 7.3, 7.9, 8.8, 9.7 nm), M(5.6, 8.4, 8.7, 9.1, 9.3, 9.8, 13.2 nm), W(6.7, 10.1, 10.7, 11.4, 12.2 nm) of the compound indicated the presence of *n*-methyl coniine. The nmr (CDCl₃) of the compound gave the following results:

0.90 δ Triplet	(J=7 Hz)	3H	C-CH ₃
2.22 δ Singlet		3H	N-CH ₃
2.76 δ Triplet	(J=4 Hz)	2H	CH ₂ -CH ₂ -N
2.88 δ Mu		1H	$\begin{array}{c} \text{N} \\ \\ \text{CH}_2-\text{CH} \\ \\ \text{CH}_2 \end{array}$

n-Methyl coniine was further identified by making its known derivatives. On boiling with hydrochloric acid a crystalline material was obtained, m.p. 187° (lit¹. 188-89°). With gold chloride it gave a yellow crystalline substance, m.p. 75° (lit¹. 77-78°). The presence of coniine was also inferred by the colour test.¹ The rest of the nitrogen containing compounds such as 1-methyl-2-pentyl-piperidine, 1-methyl-2-pentyl piperidine, etc. were identified from the com-

puterized data of mass spectrometry coupled with time programmed GLC.

The chemical composition of the essential oil of *P. acuminata* shows that the oil is mainly composed of *n*-methyl coniine and the presence of other alkaloids indicates that the species closely resembles *Conium maculatum*.¹ However, it is surprising to note that the seeds of *P. acuminata* are used as a substitute of *P. anisum* in the local market. The two species have entirely different constituents, the former being rich in *n*-methyl coniine, an alkaloid and latter containing about 80-90% anethole,⁴ a phenol ether.

These studies, therefore, present the chemistry of the *P. acuminata* for the first time.

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