

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

### Part XLII. *Bupleurum linearifolium*, D.C. (Yarguli) Seed Oil

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The essential oil of *Bupleurum linearifolium* seed, with a yield of 0.2% has been studied with respect to its physicochemical properties and chemical composition. The oil is composed of santene (6.1%),  $\alpha$ -thujene (1.9%),  $\alpha$ -pinene (2.3%), camphene (3.0%), myrcene (2.4%),  $\beta$ -phellandrene (2.8%), limonene (2.5%),  $\gamma$ -terpinene (1.5%), *p*-cymene (0.9%), an unknown ketone (1.6%), geranyl acetate (7.5%), citronellyl acetate (7.1%), a mixture of hydroxy compounds (2.0%), borneol (3.0%), bupleurol (9.0%),  $\alpha$ -terpineol (19.5%) and a mixture of coumarins (18.3%). *Bupleurum* species have been used against stomach and liver diseases. The commercial importance of the oil can only be evaluated after studying physiological effects of the oil. However, the species, which we have successfully cultivated at Murree, may be tried against liver diseases.

#### INTRODUCTION

*Bupleurum* is a large genus of about 150 species found mostly in the temperate regions of Europe and Asia. The plants are annual or perennial herbs. Only 20 species and three varieties of the genus including *Bupleurum linearifolium* have been reported to grow in Pakistan.

*Bupleurum linearifolium* grows wild in Murree, Kaghan and Swat in Pakistan. Besides their use for the ailments of the stomach and the liver, the species have been exhibited sedative, analgesic, hypothermic and antipyretic effects and are regarded as a strong central depressant [2]. No investigations have so far been carried out on the physicochemical characteristics and chemical composition of the essential oil of *Bupleurum linearifolium*, especially of the Pakistani variety. The present work has, therefore, been undertaken with a view to filling this gap in our knowledge of a medicinally useful plant of the country.

#### MATERIALS AND METHODS

The seed of *Bupleurum linearifolium* were collected from Murree Hills for these studies. The essential oil from the crushed material was recovered by dry steam-distillation according to the standard procedure [3]. After the oily layer had been separated, the aqueous distillate was extracted with diethyl ether so that water-cohabation oil was also obtained. Both essential oil and the water-cohabation oil displayed identical behaviour by TLC and IR, therefore, the two were mixed and the resultant oil studied with

respect to its physicochemical properties and chemical composition. The general methods used for the analysis of the oil have already been described in our earlier papers [3,4].

The essential oil was fractionated into hydrocarbons and oxygenated components by column chromatography using activated silica gel as adsorbent. The hydrocarbon fraction of the oil was further resolved by GLC and the individual components identified against their standard samples. The oxygenated fractions containing more than one components were rechromatographed to obtain single compounds. The various oxygenated compounds were identified by TLC, GLC and IR comparison with their authentic samples.

#### RESULTS

The percentage yield, physicochemical values and the chemical composition of the essential oil of *Bupleurum linearifolium* are recorded in Tables 1–2.

#### DISCUSSION

The essential oil of *Bupleurum linearifolium* seed possesses a reasonably sweet smell. The oil is mainly composed of oxygenated components (77% of the total oil). The hydrocarbon fraction of the oil contains monoterpenes only and no sesquiterpene was detected under the conditions given earlier. The fraction was resolved into individual components by GLC and their identification was made



Table 1. Percentage yield and physicochemical values of the essential oil of *Bupleurum linearifolium* seed.

Distillation time (hr)	8
Yield of the oil (%)	0.25 including water-cohabation oil.
Specific gravity	0.8073 <sup>17</sup>
Refractive index	1.5100 <sup>17</sup>
Optical rotation	+23° 20' <sup>17</sup>
Acid value	15.51
Ester value	30.78

Superscripts indicate the temperature at which these parameters were determined.

Table 2. Percentage composition of the essential oil of *Bupleurum linearifolium* seed.

Component	Percentage
Santene	6.1
$\alpha$ -Thujene	1.9
$\alpha$ -Pinene	2.3
Camphene	3.0
Myrcene	2.4
$\beta$ -Phellandrene	2.8
Limonene	2.5
$\gamma$ -Terpinene	1.5
<i>p</i> -Cymene	0.8
Unknown ketone	1.6
Geranyl acetate	7.5
Citronellyl acetate	7.1
Mixture of hydroxy compounds	2.0
Borneol	3.0
Bupleurol	9.0
$\alpha$ -Terpineol	19.5
Coumarins	18.3
Tarry material	7.0

by comparison method.

Elution of the column with 1% diethyl ether in n-hexane gave two components by TLC. The fraction was rechromatographed which gave geranyl acetate and an unidentified ketone. The column was then eluted with the same ratio of the solvent and a mixture of two esters was obtained. The fraction was hydrolysed with 0.1N alcoholic KOH and the parent alcohols so obtained were separated

from each other were identified as geraniol and citronellol. Thus the fraction contained geranyl and citronellyl acetates. The column when eluted with 2% diethyl ether gave a single ester by TLC and IR. The ester was citronellyl acetate. Its identification was carried out as above.

Elution of the column with 5% diethyl ether in n-hexane gave a mixture of three hydroxy compounds by GLC. Because of rather small amount of the fraction its separation into individual components was not successful. The column was, then, eluted with 10% diethyl ether in n-hexane which gave a single compound. On removal of the solvent, the fraction changed into crystalline form. The compound was identified as borneol by m.p. 210° and IR comparison. Further elution of the column with the same ratio of the solvents gave two alcohols. The two alcohols were separated from each other by preparative TLC and were identified as  $\alpha$ -terpineol and bupleurol by IR comparison.

The column was, then eluted with 20% diethyl ether in n-hexane which gave a single alcohol. It was  $\alpha$ -terpineol by TLC, GLC and IR comparison with an authentic sample of the alcohol.

Finally the column was washed with 100% diethyl ether which gave a mixture of coumarins. The fraction is still to be resolved into individual components.

Because of its valuable medicinal importance, physiological investigations on the essential oil of the species are needed to be carried out.

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#### REFERENCES

1. V.H. Heywood, *The Biology and Chemistry of the Umbelliferae* (Academic, New York 1971), p. 396.
2. Takagi, Keiji, Shibata and Modoka, *Yakugaku Zasshi*, **89**, 712 (1969); *Chem. Abstr.*, **71**, 69253 t (1969).
3. M. Ashraf and M.K. Bhatti, *Pakistan J. Sci. Ind. Res.*, **18**, 232 (1975).
4. M. Ashraf and M.K. Bhatti, *Pakistan J. Sci. Ind. Res.*, **18**, 236 (1975).