

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

Part -LI. The Essential Oil of *Bupleurum lanceolatum* Wall Seed

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The essential oil of *Bupleurum lanceolatum* Wall. in Pakistan was subjected to analysis by column, thin layer, gas chromatography and mass spectroscopy. Only the most abundant compounds representing Ca 83% of the oil were identified. The major components were hydrocarbon fraction (58.9%), oxygenated (24.1%), coumarins/tarry matter and others (17%). The essential oil has sweet smell and is recommended for use in perfumery.

Key words: *Bupleurum lanceolatum*, Umbelliferae, Essential oil, Geranylacetate.

Introduction

Bupleurum lanceolatum Wall belongs to the genus *bupleurum* of the family Umbelliferae. This genus has 150 species of which only 20 species including *B. lanceolatum* have been found in Pakistan and also have been reported to grow mostly in the temperate regions of Europe and Asia [1]. In Pakistan, it has been found growing in Kaldana (Murree Hills), district Islamabad. The plants are usually perennial or annual herbs. Some species of the genus *Bupleurum* have proved to be successful for treatment of certain stomach and liver ailments and also have shown anti-inflammatory activity against carraginan [2-4].

Literature survey revealed that no work has been done on the essential oil of this species in Pakistan. The purpose of our present investigations aims at the initiation of a long term programme with an objective to introduce novel essential oil crops for expanding Pakistani essential oil industry.

Experimental

All the reagents used were of analytical grade. GC analysis were performed on a Shimadzu, A-9 GC Model using a SE-30 fused silica capillary column, (10mx0.25 mm id) programmed from 80 to 200° at 4° /min. IR spectras were recorded on Hitachi 270-30. The plant material for our studies was collected at a mature fruiting stage.

The essential oil of *B. lanceolatum* was recovered from the crushed seeds by dry steam distillation for 12 hrs. The essential oil of *B. lanceolatum* (0.35%) was studied with respect to its physico-chemical properties according to the procedures reported in the literature [5,6].

The essential oil was subjected to fractionation by column chromatography using silica gel as an absorbant. The hydrocarbon fraction of the oil was eluted with n-hexane and diethyl ether and were identified by TLC, GC and IR by the methods described in our previous publications [6,7].

Mass spectrometer Model JMS-AX505 H combined with

Hewlet Packard gas chromatograph was used for GC/MS analysis. Data acquisition and reprocessing was performed by Jeol JMA-DA 5500 system with MS-4 BTK Library search system.

Results and Discussion

The essential oil of *B. lanceolatum* seed possesses sweet smell, with a yield of 0.35%, has been studied with respect to its physico-chemical properties and chemical composition (Table 1 and 2).

The hydrocarbon fraction (58.9%) of the essential oil of *B. lanceolatum* was obtained by the elution of the column with n-hexane. It consisted of santene (6.60%), α -thujene (8.5%), β -phellandrene (8.4%), α -pinene (9.6%), camphene (5.4%), myrcene (2.8%), limonene (5.6%), γ -terpinene (7.6%) and *p*-cymene (4.4%). The MS analysis showing relative intensities of the major peaks is given in Table 2. Monoterpenes showed similarity between their spectra but difference in the abundance of the corresponding ions in their spectra are readily apparent. The parent molecular ion (136+) of the monoterpenes showed the fragmentation pattern as supported by metastable transitions, of the form:

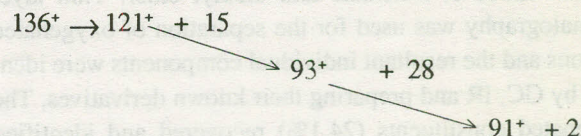


TABLE 1. PERCENTAGE YIELD AND PHYSICO CHEMICAL VALUES OF THE ESSENTIAL OIL OF THE MATURE SEEDS OF *BUPLEURUM LANCEOLATUM*.

| | |
|------------------|--------------------------------------|
| Yield | 0.35% (after 12 hrs of distillation) |
| Specific gravity | 0.806019 |
| Refractive index | 1.5180 |
| Acid value | 16.12 |
| Ester value | 22.87 |

TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OIL OF *BUPLEURUM LANCEOLATUM* SEED.

| Components | Percentage | m/z |
|------------------------------------|------------|------------------------|
| Santene | 6.6 | 27,44,93,77,120,136 |
| α -Thujene | 8.5 | 93,69,41,27,79,127 |
| β -Phellandrene | 8.4 | 27,44,43,67,93,127,136 |
| α -Pinene | 9.6 | 93,77,41,121,136,127 |
| Camphene | 5.4 | 121,107,93,79,43,68 |
| Myrcene | 2.8 | 93,69,41,27,79,43 |
| Limonene | 5.6 | 27,41,43,67,93,127 |
| γ -Terpene | 7.6 | 27,44,93,77,120,136 |
| <i>p</i> -Cymene | 4.4 | 119,93,77,55,42,27 |
| Gereneol | 5.6 | 76,92,103,131,149,164 |
| 4-Terpineol | 6.3 | 71,11, 93,154,41 |
| Geranyl acetate | 6.4 | 43,92,136,94,121 |
| Terpenyl acetate | 5.8 | 43,136,93,121,94 |
| Others, coumarins and tarry matter | 17.0 | (Unidentified) |

But in some cases except limonene and myrcene, a metastable transition corresponding to the loss of 43 mass units as a single entity in the monoterpenes $136^+ \longrightarrow 93^+ + 43$, is hard to explain. Weinburg and Djerassi [8] made detailed investigation and concluded that the loss of 43 mass units could be explained by the migration of double bonds. In β -phellandrene such a behaviour is easily explained because of the properties of allylic fission. In limonene the favoured process is $94^+ \longrightarrow 79^+ + 15$. The assignment of a molecular structure to a given cracking pattern is no doubt a matter of considerable difficulty but could be resolved by considering; (i) The molecular weight and formula of a compound. (ii) The base peak and (iii) The general fragmentation pattern which enable the class of compound to be identified.

The present observations accord well with the published data [9,10]. The composition has been found very similar to the preliminary composition studies of *B. gibraltarium*.

The oxygenated components of the oil were eluted with different ratios of *n*-hexane and diethyl ether. Thin layer chromatography was used for the separation of oxygenated fractions and the resultant individual components were identified by GC, IR and preparing their known derivatives. The oxygenated constituents (24.1%) recovered and identified were geraneol (5.6%), terpineol (6.3%), geranyl acetate (6.4%) and terpenyl acetate (5.8%) which were eluted with 1% diethyl ether in *n*-hexane (ms analysis, Table 2) and rest of the fraction constituted mixture of coumarins, tarry matter and others

(17.0%). These are reported as unidentified by GC/MS studies.

The essential oil of *B. lanceolatum* has comparable composition to *B. linearifolium*, *B. gibraltarium*, *B. stewartianum* and *B. tenuis*. [7,11,13,14]. The hydrocarbon fraction of the four species are composed of almost identical constituents.

The ester fraction constitute only two esters i.e. geranyl acetate and terpenyl acetate which are also present in *B. linearifolium*, *B. stewartianum*, *B. gibraltarium* and *B. tenuis*.

Due to the presence of acceptable sweet smell the essential oil of *B. lanceolatum* can find application in perfumery.

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