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

Part VI. Anethum Graveolens (Dill, Sowa) Seed Oil

MUHAMMAD ASHRAF, JAVED AZIZ and MUHAMMAD KHURSHID BHATTY

PCSIR Laboratories, Lahore

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Abstract. The essential oil of the Pakistani *Anethum graveolens* seed, has been studied for the first time with respect to its yield, physico-chemical characteristics and chemical composition. The yield of the oil when distilled from fresh seed is 2.5%. The oil is composed of 15.82% hydrocarbons and 84.18% oxygenated components, the former being limonene (9.34%) and phellandrene (6.48%) and the latter carvone (52.25%) and dillapiole (28.28%) of the total oil. The content and quality of the oil are of International standard and qualify it as a valuable raw material of the country.

Anethum graveolens, an Umbellifer commanding world-wide distribution as cultivated and wild species, is grown in Pakistan in sizeable quantities. Because of the plant's extensive occurrence and usage, the essential oil of its seed has been the subject of numerous studies.[1-12] It is unfortunate, however, that the oil of the Pakistani species has not been studied so far even though the seed has been used as an important flavouring and therapeutic agent.[13] Because of its commercial significance, the essential oil of the seed of the local species has, therefore, been investigated and the details of the studies are presented in this paper.

Experimental

Materials and Methods. Fresh and mature seed of the cultivated *Anethum graveolens* were collected from the field and employed for this work. The material was crushed completely and distilled with dry steam.[14] The oil was recovered in two fractions i.e., lighter than water and heavier than water. The general methods used in these studies have been described in Parts 1 and 2 of this series.[15]

The material resulting from the combination of the two fractions, mentioned above, was analysed by column chromatography using activated alumina (Brockmann, activity, II, III, E. Merck). A Phase Sep. GLC machine with a copper column packed with 20% polyethylene glycol succinate (BDH) coated on celite (60-80 mesh, nitrogen as carrier gas and flame ionisation detector, operated at 110°, was used for the resolution and identification of the hydrocarbon components of the oil. The oxygenated fractions containing more than one component were rechromatographed and the components identified by IR comparison with their authentic samples and also by converting them into known derivatives.

Results

The physicochemical values and the chemical composition of the oil are recorded in Tables 1 and 2.

Discussion

The physico-chemical properties were determined according to the normal procedure[1,2] for this oil ; the physical values were defined in terms of the two fractions separately while the chemical values were estimated on the material obtained by the combination of the two fractions.

The components of the hydrocarbon fraction, eluted from the column with n-hexane, were identified and estimated by means of GLC (Fig. 1) using known reference compounds. The oxygenated components of the oil were eluted successively with 3%, 10% and 50% diethyl ether in n-hexane.

The major compounds identified in the present work are essentially the same as reported by earlier worker.[2,3,6,7,11] The oil does not contain sesquiterpenes and no earlier workers have reported any till recently. Limonene and phellandrene constitute the major hydrocarbons of the oil; where as the presence of the former has been indicated by all the previous workers, that of the latter has been shown by Handa *et al.*[6] and Gladstone[7] only. Our studies show the presence of both the hydrocarbons in the Pakistani oil. Our results are in agreement with those of the earlier workers regarding the absence of α-pinene in the oil with the only exception of Gladstone[7] who, however, indicated the presence of this hydrocarbon in this oil.

Only Malvayia and Dutta[2] have reported the presence of eugenol, thymol and anisole in the oil. We nevertheless, were not able to establish the existence of these compounds in the Pakistani oil.

TABLE 1. PERCENTAGE YIELD AND PHYSICOCHEMICAL PROPERTIES OF THE ESSENTIAL OIL OF *Anethum graveolens* THEIR COMPARISON WITH THE VALUES OF SIMILAR OILS PRODUCER ELSEWHERE.

Constant	Present work		Rao *et al.*[1]		Malaviya and Dutta [2]	
	Fraction		Fraction		Fraction	
	Heavy	Light	Heavy	Light	Heavy	Light
Yield *	2.7%		—		—	
Colour *	Yellow		—		—	
Odour *	Pleasant		—		—	
Taste *	Sweet		—		—	
Specific gravity	1.0396 ^{27}	0.9494 ^{20}	1.0935 ^{20}	0.9313 ^{20}	1.0573 ^{20}	0.9719 ^{20}
Refractive index	1.5134 ^{27}	1.4955 ^{22}	1.5154 ^{20}	1.4853 ^{20}	1.4905 ^{20}	1.0573 ^{20}
Optical rotation	+23°12 ^{27}	+50° 12 ^{27}	—	+58°.2	+23.C°	+38.5°
Acid value*	0.576	—	—		—	
Ester value *	12.620		—		—	

*On the basis of the total oil including water cohobation oil (0.27%), lighter than water fraction (1.8%) and heavier than water fraction (0.7%). The superscripts indicate the temperature in C at which these parameters where taken.

TABLE 2. CHEMICAL COMPOSITION OF THE ESSENTIAL OIL OF THE SEED OF *Antheum graveolens* GROWN IN PAKISTAN AND ITS COMPARISON WITH THE COMPOSITION OF SIMILAR OILS PRODUCED ELSEWHERE.

Constituent	Present work	Malaviya & Dutt[2]	Gupta *et al.*[3]	Handa *et al.*[6]	Gladstones[7]	Bhattacharyya[11] *et al.*
α-Pinene	ND	ND	ND	ND	D	ND
Limonene	9.34%	9.00%	23.24%	D	D	34.40%
Phellandrene	6.48%	ND	ND	D	D	ND
Dillapiole	28.28%	39.60%	19.20%	D	ND	18.90%
Carvone	52.25%	46.50%	41.70%	53.00%	40.60%	30.00%
Hydroxy compounds	1.80%	—	—	—	—	—
Unrecovered material	1.75%	—	—	—	—	—
Dihydrocarvone	D	ND	ND	ND	D	0.10%
Eugenol	ND	Traces	ND	ND	ND	ND
Anisole	ND	,,	ND	ND	ND	ND
Thymol	ND	,,	,,	ND	ND	ND

D; Detected, ND: Not Detected.

Fig. 1. Chromatogram of *Anethum graveolens* hydrocarbon run at 140° using PEGS column.

The two major oxygenated components identified in the present work are dillapiole and carvone. Dillapiole was identified by IR and by preparing its mono-bromospiole-dibromide derivative,[15] m.p. 105-106° (lit[16]. 107°), carvone was identified by IR and by preparing its semicarbazone derivative, m.p. 160° (lit[17]. 162°). The rest of the oxygenated fraction was hydroxy in nature by IR, but its complete identification awaits further work.

The present studies show that the Pakistani oil consists of linonene, phellandrene, carvone and dillapiole constituting some 96% of the oil. The minor variation in its composition from similar other oils may be attributed to climatic conditions, quality of soil and the methods of analysis. It has thus been found that the Indian *A. graveolens* when sown in Europe culminated in such plants whose essential oil did not have dillapiole, which is an important constituent of the Indian dill seed oil.

A genuine *A. graveolens* seed essential oil should not contain a constituent boiling at so high a temperature as 285° and should have no portion which is heavier than water. Because of these constraints, the oil obtained from the dill seed grown in Pakistan has not been accepted officially as such. However, the essential oil can easily be freed from dillapiole and the residual material which still amounts to 72% of the total oil, with a corresponding yield of 1.8%, can become an oil of the acceptable quality.

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