Technology Section

Pakistan J. Sci. Ind. Res., Vol. 20, No. 2, April 1977

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

Part VIII. Carum Carvi Linn. (Caraway, Kala Zira) Oil of the Mature and the Immature Seeds and the Whole Immature Plant

AMNA KARIM, MUHAMMAD ASHRAF, MASOOD PERVEZ and MUHAMMAD KHURSHID BHATTY

PCSIR Laboratories, Lahore

(Received July 14, 1976; revised April 28, 1977)

Abstract. The essential oil of *Carum carvi* Linn, distilled from the mature seed, immature seed and whole plant of the Pakistani origin in 3.5%, 6.7% and 0.52% yield respectively has been characterized for the first time. In the order of the three materials it contains α-pinene (0.3, 0.9 and 0.2%), camphene (0, 1.5 and 0.3%) β-pinene (0.9, 1.0 and 0.2%), myrcene (0.6, 2.7 and 1.5%), Δ^3-carene (0, 0.3 and 1.0%), limonene (26.2, 30.2 and 4.2%), γ-terpinene (1.8, 23.6 and 2.7%), *p*-cymene (2.1, 5.6 and 0.3%), *dl*-cadinene (0, 0 and 37.2%), myristicin (0.7, 0.2 and 1.2%), mixture of carveol acetate and dihydrocarveol acetate (0, 0.3 and 1.1%), dihydrocarvone (2.5, 0.8 and 2.3%), carvone (58.3, 31.4 and 31.2%), terpinene-4-ol (0, 0 and 1.2%), dihydrocarveol (1.2, 1.2 and 9.5%), perillyl alcohol (0, 0 and 1.6%) and carveol (4.1, 0.4 and 2.2%). The caraway oil from the plants grown in Pakistan is similar to that produced in other countries.

Carum carvi Linn (caraway, kala zira) is widely cultivated in many temperate countries of the world because of the commercial importance of its seed and essential oil.

In Pakistan it grows wild in Chitral, Gilgit, Baltistan and Kaghan from where its seed is collected and despatched at fairly high prices for use as an important ingredient of curries. It is noteworthy that the seeds of *Bunium persicum* Boiss and *Bunium cylindricum* Boiss which are also species of *Umbelliferae* though distinctly different from *Carum carvi* are erroneously called Siah zira and used in its place.

The commercial importance of the whole seed as also of the essential oil of caraway is rather high from the industrial and medicinal points of view. The seed is primarily used for flavouring a variety of ebibles and beverages[1] while its essential oil is used in the preparation of soaps and as a medicine.[2–4]

Unfortunately, no attention has been given to the cultivation of this species on a commercial scale in Pakistan. Some 100-125 tons of the seeds of the wild growing caraway plants are, nevertheless, collected in the months of September and October every year to meet the local requirements. Furthermore, because it could prove profitable as a crop, it can successfully replace relatively cheaper crops such as corn in the areas of its natural habitat.

No investigations have so far been carried out on the physico-chemical characteristics or on the chemical composition of the caraway essential oil of Pakistan. The present work has, therefore, been pursued with a view to filling this gap in our knowledge of a potentially useful raw material of the country.

Experimental

Materials and Methods. The mature and immature seeds and the whole immature plant of *Carum carvi* were directly collected from the Kaghan valley. The essential oil from the crushed material was distilled by dry steam.[5] The instruments used in the determination of the various characteristics of the oil have already been reported.[5] Chemical values of the oil were determined according to Guenther.[6]

The oil was fractionated into hydrocarbons and oxygenated components by chromatography using silica gel as an adsorbent. The hydrocarbon fraction was further resolved into terpenes by GLC using 3mm × 3m copper column packed with 7.5% carbowax on chromosorb (acid washed), nitrogen as carrier gas and flame ionisation detector. The column temperature was maintained at 120°. The oxygenated components were identified by IR and conversion into their known derivatives.

Results

The physicochemical properties and the chemical composition of the essential oil are described in Tables 1 and 2.

Discussion

The yield and physicochemical properties of the essential oil as obtained from the mature and the immature seeds of the Pakistani caraway are comparable with those recorded for similar oils in literature[1] (Table 1). Qualitatively, the constituents

of the mature seed essential oil are also largely the same as those of similar oils produced elsewhere and reported in literature[1,8–12] (Table 2).

Ikeda *et al.*[8] have shown the oil of caraway to contain 38% terpenes of which limonene constitutes almost 100% with traces of seven more monoterpenes. The oil of the Pakistani caraway, however, displays superior quality in the sense that it contains a lesser amount of terpenic fraction and is relatively more rich with respect to oxygenated components. Koul and Nigam[9] using column chromatography found the Indian oil of the mature seed

TABLE 1. PERCENTAGE YIELD AND PHYSICOCHEMICAL CONSTANTS OF THE *C. carvi* ESSENTIAL OIL FROM THE MATURE AND THE IMMATURE SEED AND THE WHOLE PLANT GROWN IN PAKISTAN.

Constant	Present work			Literature[7]	
	Mature seed	Immature seed	Whole Immature plant	Immature seed	Mature seed
Yield (max)	3.5%	6.7%	0.52%	—	4—6%
Time	12 hr	12 hr	12 hr *	—	10 hr
Specifi gravity	$0.907^{22.5}_{1}$	0.813^{32}_{6}	0.901^{31}_{6}	0.863^{20}_{6}	0.907 — 0.919^{15}_{6}
Refractive index	1.486^{21}_{D}	1.481^{32}_{D}	1.485^{31}_{D}	—	1.484 — 1.488^{20}_{D}
Optical rotation	$+69°\ 14'^{21}_{D}$	$+79°\ 24'^{32}_{D}$	$+30°\ 16'^{31}_{D}$	+78°0′	+70° 0′ — 81° 0′
Acid value	1.5	0.34	3.5	—	—
Ester value	3.5	6.7	45.4	—	—
Ester value after acetylation	25.2	13.2	73.2	—	—

*Distillation time for the fresh whole plant is considered to be higher than needed. The superscript indicate temperature in C at which these parameters were determined.

TABLE 2. CHEMICAL COMPOSITION OF THE *C. carvi* ESSENTIAL OIL OBTAINED FROM THE MATURE AND IMMATUR SEEDS AND THE WHOLE PLANT GROWN IN PAKISTAN.

Eluent	Constituent	Mature seed %	Immature seed %	Whole plant %	Literature[1, 8-12] mature seed
n-Hexane	Hydrocarbons *	31.9	65.7	47.6	+
	α-Pinene	0.3	0.9	0.2	+
	Camphene	—	1.5	0.3	—
	β-Pinene	0.9	1.0	0.2	+
	Myrcene	0.6	2.6	1.5	+
	Δ^3-Carene	—	0.3	1.0	+
	Limonene	26.2	30.2	4.2	+
	γ-Terpinene	1.8	23.6	2.7	—
	p-Cymene	2.1	5.6	0.3	+
n-Hexane	*dl*-Cadinene	—	—	37.2	—
1% Diethyl ether in n-hexane	Myristicin	0.7	0.2	1.2	—
2% Diethyl ether in n-hexane.	Carveol acetate and dihydro Carveol acetate	—	0.3	1.1	—
3% Diethyl ether in n-hexane	Dihydrocarvone	2.5	0.8	2.3	+
5% Diethyl ether in n-hexane	Carvone	58.3	31.4	31.2	+
6% Diethyl ether in n-hexane	Terpinen-4-ol	—	—	1.2	+
7% Diethyl ether in n-hexane	Dihydro carveol	1.2	1.2	9.5	+
8% Diethyl ether in n-hexane	Perillyl alcohol	—	—	1.6	+
10% Diethyl ether in n-hexane	Carveol	4.1	0.4	2.2	+
20% Diethyl ether in n-hexane	Carveol and mixture of three unidentified alcohols (4:1)	1.3	—	2.1	—

* Resolved by GLC.

to contain limonene only; while Atal and Sood[10] reported the presence of α-pinene and *p*-cymene as well with the help of GLC. Our results are quite in agreement with those of the Indian investigators, except that the Pakistani mature seed contains α-pinene, myrcene and γ-terpinene. Yin *et al.*[11] using GLC have identified α-pinene, β-pinene, myrcene, limonene, γ-terpinene and *p*-cymene in the caraway oil. It is probable that even the Pakistani oil might also contain the terpenes found in other similar oils, but their amount is so small that it could not be detected under our experimental conditions.

Myristicin which has been isolated for the first time in caraway oil (Table 2) was characterised by the comparison of its IR with that of an authentic sample and by converting it into dibrimo myristicin dibrimide, m.p. 128-129° (Ethanol) (lit.[12] 130°). The acetates in the oil were identified by hydrolysing them into the carveol and dihydrocarveol whose IR spectra are known. No acetate was, however, detected in the mature seed essential oil.

Dihydrocarvone and carvone were found to be present in the oil. The compounds were identified through the preparation of 2, 4-dinitrophenyl hydrozones of dihydrocarvone and carvone m.ps; 153—154 (lit.[13] 153°) and 189—190° (lit.[7] 189) and semicarbazones m.ps. 188—189° (lit.[7] 189—191°) and 160—162° (lit.[7] 162°) respectively

Four hydroxy compounds namely terpinen-4-ol, dihydrocarveol, perillyl alcohol and carveol were characterised in the oil by direct comparison of their IR with those of the authentic samples as also by oxidising them to carbonylic compounds and converting them into 2, 4—dinitrophenyl hydrazones. Terpinen-4-ol and perillyl alcohol was detected in the whole plant oil only. Besides these, the essential oil of the mature seeds and the whole plant also contained small amounts of a mixture of three hydroxy compounds which have as yet to be identified.

According to Guenther,[1] traces of acetaldehyde, methanol, furfural, diacetyl, dihydrocarvone, carveol, dl-dihydrocarveol, neodihydrocarveol isodihydrocarveol, perillyl alcohol and dihydropinol are also present in addition to carvone in the oil of caraway. El Deeb *et al.*[14 15] nevertheless, showed that the oxygenated constituents of the oil consisted of carvone and citral and indicated the presence of methyl salicylate and eugenol in addition.

During the present investigations we could not detect any citral, methyl salicylate and eugenol in the oxygenated fraction. Atal and Sood[10] showed carvone as the only oxygenated constituent present in the Indian caraway oil. Kaul and Nigam[9] found dihydrocarvone and carveol as well. We have isolated these compounds from the Pakistani caraway oil also. Hans[16] had reported the presence of linalool, dihydrocarveol and perillyl alcohol in an European species but we could not detect linalool in our caraway oil.

Yin *et al.*[11] using GLC were able to identify carvone *cis*- and *trans*-dihydrocarvone, 1—p—menthene-4-ol and different isomers of dihydro carveol. But we have not yet been able to resolve our dihydrocarveol fraction into its isomeric components.

From the above studies it can be concluded that the physico-chemical characteristics and chemical composition of the Pakistani caraway seed oil are similar to such oils produced elsewhere in the world and thus qualify it to be an important commercial commodity of the country.

Acknowledgement. We are grateful to the United States Department of Agriculture for financing this research under a PL -480 Scheme and Mr. Abdul Waheed Sabir, our Botanist, for the procurement of authentic materials for the studies.

References

1. E. Guenther, *The Essential Oils* (D. Van Nostrand Company, Inc., New York, 1948), vol. IV, p. 573.
2. A. Koscik, Roczniki Akad, Med. Biolymstoku, **1**, 227 (1955) Chem. Abstr., **48**, 10128 (1954).
3. J. C. Maruzzella and L. Ligouri, J. Am. Phar. Assoc., **47**, 250 (1958).
4. V. H. Heywood, *The Biology and Chemistry of the Umbelliferae* (Academic Press, New York, 1971), p. 385.
5. M. Ashraf and M. K. Bhatty, Part 1 of this Series, Pakistan J. Sci. Ind. Res., **18**, 5 (1975).
6. E. Guenther, *The Essential Oils* (D. Van Nostrand Company Inc., New, York, 1948), vol. 1, p. 273.
7. E. Guenther, *The Essential Oils* (D. Van Nostrand Company Inc., New York, 1948), vol. II, p. 412.
8. R. M. Ikeda, W. L. Stanley, S. H. Vannier and E. M. Spitlar, J. Food. Sci., **27**, 455 (1962).
9. G. L. Koul and S. S. Nigam, Perfumery Essent. Oil Record, **57**, 91 (1966).
10. C. K. Atal and N. M. Sood, Indian J. Pharm., **29**, 42 (1966).
11. Y. Yin, N. Zarghani and D. E. Heinz, J. Food Sci., **35**, 531 (1970).
12. E. Guenther, *The Essential Oils* (D. Van Nostrand Company Inc., New York, 1948), vol. II, p. 531.
13. T. Ueda and Y. Fujita, Nippon Kagaku Zesshi, **78**, 658 (1957); Chem. Abstr., **53**, 3609a (1959).
14. S. R. El-Deeb, M. S. Karawaya and S. K. Wahba, J. Pharm. Sci. (U.A.R.), **3**, 81 (1962).
15. S. R. El-Deeb, M. S. Karawaya, S. K. Wahba and F. M. Ebeid, J. Pharm. Sci. (U.A.R.), **4**, 63 (1962).
16. K. Hans, Riechst. Aromen. Koerperflegem, **19**, 65 (1969); Chem. Abstr., **71**, 79917b (1969).