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

Part IX. Daucus carota (Carrot, Gajor) Seed Oil

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Abstract. The essential oil of the Pakistani red, black and yellow *Daucus carota* seeds, obtained in 2.1, 2.0 and 1.3% yield has been studied for the first time for its physicochemical properties and chemical composition. The composition of the oil recorded in the order of the varieties is α-pinene (1.15, 0.45, 0.30%,) camphene (0.08; traces, 0%), myrcene (1.40, 2.5, 0.1%), an unidentified monoterpene (0.1, 0.35, 0%), Δ^3-carene (0.30, 1.2, 0%) limonene (2.0, 3.1, 1.2%), β-bisabolene (7.25, 7.53, 3.52%), unknown sesquiterpenes (11.67, 3.98, 2.0%), caratol (62.8, 64.9, 77.52%), unidentified hydroxy compound (2.6, 3.4, 5.26%) and daucol (1.5, 0, 3.91%). The essential oil from the Pakistani *D. carota* is one of the best oils produced in the world.

Daucus carota, a common edible vegetable, is a widely distributed species in the world. Its varieties as characterised by the colour of their roots are variable morphologically also[1].

The vegetable is recognised as a valuable food adjunct, if not the whole food itself. Its roots are locally consumed in the form of spiced dishes, halvahs and pickles. In countries where the food industry is more advanced, it is extensively used for processing canned, frozen and dehydrated products for sweetening and flavouring. Its roots are employed as coffee substitute and sometimes as colouring agent for butter. Medicinally, its attributes are varied and large.[2]

The essential oil of *D. carota* produced in some parts of the world has thoroughly been investigated[3–8] but that of the Pakistani species has not so far been studied even though carrot is extensively cultivated in the country. In order, therefore, to fill this gap in our knowledge of the local resources, the oil of the Pakistani species has been examined.

Experimental

Materials and Methods. Fresh seeds of the red, black and yellow varieties of carrot were procured locally. The essential oil was recovered by dry steam distillation of the crushed materials.[9] The general method employed for these studies have been described in Parts 1 and 2 of this series.

The oil was analysed by column chromatography using activated alumina (Brockmann, activity II, III, E. Merck) Resolution of the hydrocarbon fraction into individual constituents was affected by GLC using a copper column (3 mm x 3 m) packed with 20% polyethylene glycol succinate on celite (60-80 mesh), nitrogen as carrier gas flame ionisation detector and operated at 170°. The oxygenated components were identified by the comparison of their IR with those of the authentic samples and also by converting them into their known derivatives. The essential oils of the red variety of *D. carota* seed was also examined by time programmed GLC coupled with mass spectrometery using glass column (0.25″ × 6′) packed with 3% silar 5 cp (Fig. 1).

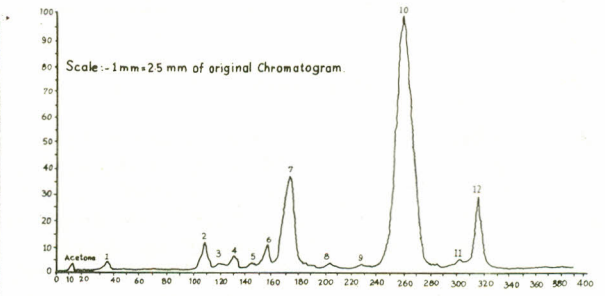

Fig. 1. Time programmed GLC of *Daucus carota* essential oil using 3% silver 5 cp glass column (0.25″x 6′).

Results

The physicochemical values and the chemical composition of the essential oil of the three varieties of the *D. carota* seed is recorded in Table 1 and 2.

TABLE 1. COMPARATIVE YIELDS AND PHYSICOCHEMICAL PROPERTIES OF THE ESSENTIAL OIL OF THE SEEDS OF *Daucus carota* VARIETIES.

Constant	Red carrot	Black carrot	Yellow carrot
Yield	2.1%	2.0%	1.3%
Time	10 hr	10 hr	10 hr
Specific gravity	0.9016^{21}	0.9384^{21}	0.9568^{21}
Refractive index	1.4160^{21}	1.5022^{22}	1.4970^{22}
Optical rotation	+14° 45′	+14° 0′	+17° 14′
Acid value	1.12	0.51	0.93
Ester value	3.40	10.29	6.20
Ester value after accetylation	57.20	19.30	31.13

The superscripts indicate temperature in C at which these parameters were determined.

TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OIL OF *Daucus carota* SEED AS DETERMINED BY COLUMN CHROMATOGRAPHY.

Solvents used	Component	Red carrot %	Black carrot %	Yellow carrot %
n-Hexane	Hydrocarbons*	30.19	28.60	10.07
	α-Pinene	1.15	0.45	0.30
	Camphene	0.08	Traces	—
	Myrcene	1.40	2.50	0.10
	Unknown monoterpene	0.10	0.35	—
	$\triangle^3$-Carene	0.30	1.20	—
	Limonene	2.00	3.10	1.20
	β-Bisabolene	7.25	7.53	3.52
	Unknown sesquiterpene	2.34	3.10	—
	β-Caryophyllene	2.14	1.34	—
	β-Selinene	4.10	3.15	2.95
	Unknown sesquiterpene	6.23	4.03	2.00
	—do—	3.10	1.85	—
20% to 25% Diethyl ether in n-Hexane	Caratol	62.80	64.90	77.52
50% Diethyl ether in n-Hexane	Mixture of three hydroxy componds	2.60	3.40	5.26
50% to 100% Diethyl ether in n-Hexane	Daucol	1.50	—	3.91
	Unrecovered material	2.91	3.10	3.24

* Resolved by GLC.

Discussion

Many references in literature describe[3–8] the chemical composition of the essential oil of the seed of *Daucus carota*. The sesquiterpenic alcohol, caratol, has been shown to be always present in the essential oil of this species but there is lack of agreement regarding the presence or absence of other constituents which suggests that the composition of carrot seed oil varies from variety to variety not only qualitatively, but also quantitatively, thus reflecting not only varietal differences, but also those due to the methods of analysis.

The essential oil from the carrot seed in the present work was separated into hydrocarbon and oxygenated components by column chromatography; the hydrocarbon fraction being resolved into mono- and sesquiterpenes by GLC analysis of the monoterpene sub-fraction gave six distinct peaks because of the enrichment effect. Previously, the detection of all the terpenes by the GLC of the whole oil had been difficult because of their being over shadowed by the larger constituents of the oil.

The presence of α-pinene, β-pinene, limonene and an unknown monoterpene as shown by Zalkow *et al.*[10] in the essential oil of *D. carota* seed supports our method of analysis. Our results are further supported qualitatively by Earle *et al.*, who analysed our oil of the red variety as such by time-programmed GLC (Table 3). However, we were unable to identify longifolene and bergamotene which these workers had identified, although it is possible that the unknown peaks in our analysis (Table 2) might well be these hydrocarbons.

The second major fraction as isolated by column chromatography was identified as caratol. It is the main smelling substance of the oil. The amount of caratol in the three varieties is different as determined by column chromatography. A survey of literature shows the presence of different amounts of caratol, the sesquiterpenic alcohol in the oils of this species. For example the essential oil of the Indian black carrot seed has been claimed to be one of the best oils containing 70% caratol. If this is the criterion, then the Pakistani yellow carrot seed essential oil which contains 77.5% of caratol, is even better than that of the Indian variety.

The third fraction of the oil was a mixture of five compounds (by TLC) in which one was caratol. IR analysis of this fraction showed the presence of hydroxy and carbonyl compounds. We have not been able to isolate and identify the components of this fraction entirely. However, the oil analysis by GLC using 0.25" x 6' glass column packed with 3% silar 5 cp showed the presence of elemol/eudesmol (Table 3).

The last fraction consisted of daucol. Zalkow *et al.*[11] have also reported the presence of 2.0% daucol which amount is nearly the same as ours. In contrast, Nigam *et al.*[8] have reported twice the amount

TABLE 3. PERCENTAGE COMPOSITION OF THE ESSENTIAL OIL OF THE *D. carota* RED VARIETY SEED DETERMINED ON A TIME PROGRAMMED GLC. *

Component	Percentage
Limonene	0.40
Longifolene	4.00
Unknown sesquiterpene	0.50
Bergamotene	1.66
β-Bisabolene	0.50
β-Caryophyllene	3.30
β-Selinene	16.10
Unknown sesquiterpene (M.W. 204)	0.20
—do—	0.01
Caratol	67.24
Klemol/cudesmol	0.87
Daucol	5.77

*This analysis was done for us by the courtesy of M/s Earle, F.R. & Kleiman, R. of the Agriculture Research Service, Northern Peoria Regional Research Laboratory, Peoria, Illinois, U.S.A.

of daucol in the Indian oil.

In the present work the essential oil from the three varieties has nearly identical physico chemical properties (Table 1). The IR (2.9, 3.45, 7.0, 7.35, 8.2, 8.6, 9.0, 9.35, 9.8, 10.0, 11.3, 12.2, 12.2, μm) of all the varieties are also identical. From the analysis of the three oils, the following conclusion can be drawn :

Firstly, the oil of the red and black carrot seed has similar percentage of hydrocarbon fractions. Secondly, the percentage of caratol which determines the quality of the oil is the same in the black and red, but it is higher in the yellow carrots. Thirdly, the percentage of the hydroxy and carbonyl compounds is nearly the same in all the varieties. Finally, the oil of the black variety does not contain any daucol and the amount of caratol in the yellow variety is the highest.

The results of the present studies clearly indicate that the essential oil from the Pakistani *Daucus carota* is one of the best oils produced in the world.

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