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

Part XXIX. *Ducrosia anethifolia* (DC) Boiss. (Kamyan) Seed Oil

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Abstract. The physico-chemical characteristics and chemical composition of the essential oils, steam distilled from the mature seed of *Ducrosia anethifolia* collected from Quetta and Nushki (yield 1.5%, 1.0%) and immature seed from Nushki (yield 2.1%), have been determined for the first time. The three oils respectively contain α-thujene (0.08, 0.05, 0.05%), α-pinene (1.10, 0.72, 0.66%), camphene (0.24, 0.15, 0.14%), myrcene (0.59, 0.39, 0.35%), limonene (0.82, 0.53, 0.49%), γ-terpinene (0.15, 0.10, 0.09%), *p*-cymene (0.41, 0.27, 0.24%), 1-methyl-4-isopropenyl benzene (0.08, 0.05, 0.05%), α-cederene (0.18, 0.12, 0.10%), an unknown sesquiterpene (1.28, 0.83, 0.76%), β-caryophyllene (0.32, 0.21, 0.20%), β-elemene (0.23, 0.15, 0.14%), α-farnesene (0.13, 0.08, 0.08%), δ-cadinene (0.85, 0.56, 0.50%), β-selinene (1.14, 0.75, 0.68%), unknown sesquiterpenes (0.90, 0.57, 0.51%), β-bisabolene (0.10, 0.07, 0.06%), *cis*-chrysanthenyl acetate (58.50, 61.30, 52.30%), boronyl acetate and chrysanthenone (3.0, 4.20, 0.60%), citronellyl acetate (13.40, 10.70, 25.30%) and a mixture of an ester and a hydroxy compound (15.20, 15.70, 15.00%).

A noteworthy feature of this composition is that the occurrence of *cis*-chrysanthenyl acetate in the *Umbelliferae* species is quite novel.

Introduction

Ducrosia is a genus of 5-6 species found in Afghanistan, Middle East and Pakistan. Only two species namely *Ducrosia anethifolia* and *Ducrosia avatiloba* are reported to grow wild in Pakistan. The plants are annual herbs.

Ducrosia anethifolia is distributed in the North West Frontier and Baluchistan Provinces. It has also been cultivated successfully by us in Quetta, Murree and Lahore. The plant is locally used as a fodder for sheep and camels.

The present work has been undertaken with a view to determining the quality and chemical composition of the essential oil recovered from the seeds of *Ducrosia anethifolia*.

Experimental

Materials and Methods. Mature and immature seeds of *Ducrosia anethifolia* were hand-collected from the Baluchistan Province. The essential oil from the crushed materials was obtained by dry steam distillation according to the standard procedure.[1] The general methods employed for these studies have already been communicated.[1,2] Besides these methods, GLC/MS was used for the resolution and identification of the hydrocarbon fraction of the oil and NMR for the structure elucidation of the major ester.

Chromatographic Analysis of the Oil. The oil was fractionated into hydrocarbons and oxygenated components by column chromatography using silica gel as an adsorbent. The hydrocarbon fraction of the oil was eluted from the column with n-hexane and further resolved into individual components by time and temperature programmed GLC/MS using a glass column (0.25" x 6') packed with 3% silar 5 cp. Identification of the various constituents was made from the mass spectra. The oxygenated components of the oil were separated from the column by using different proportions of diethyl ether in n-hexane and the components, thus

obtained were identified by IR, TLC, GLC, NMR and also by preparing their known derivatives.

Results

The percentage yield, physico-chemical values and chemical composition of the three essential oils of *Ducrosia anethifolia* are given in Tables 1 and 2. The GLC resolution of the hydrocarbon fraction of the essential oil is shown in Fig. 1.

TABLE 1. PERCENTAGE YIELD AND PHYSICOCHEMICAL VALUES OF THE ESSENTIAL OIL OF *Ducrosia anethifolia* SEEDS.

Yield & values	Mature seed from		Immature seed from
	Quetta	Nushki	Nushki
Distillation period	16 hr	16 hr	16 hr
Yield of oil	1.5%	1.0%	2.1%
Specific gravity	0.9562^{16}	0.8648^{16}	0.8390^{24}
Refractive index	1.4725^{16}	1.4770^{16}	1.4740^{22}
Optical rotation	$+4^{o}30'^{16}$	$+4^{o}38'^{16}$	$+5^{o}6'^{22}$
Acid value	1.20	3.05	4.80
Ester value	259.00	233.00	269.00

The superscripts indicate the temperature at which these parameters were determined.

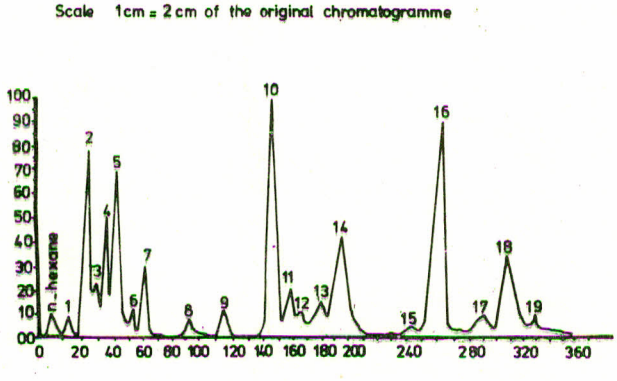

Fig. 1. Showing time and temperature programmed GLC of the hydrocarbon fraction of the essential oil of *Ducrosia anethifolia* using 3% silar 5 cp glass column (0.25" x 6').

TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OILS OF *Ducrosia enethifolia* SEEDS.

Component	Mature seed from		Immature seed from
	Quetta	Nushki	Nushki
	%	%	%
Hydrocarbons*	8.60	5.60	5.10
α-Thujene	0.08	0.05	0.05
α-Pinene	1.10	0.72	0.66
Camphene	0.24	0.15	0.14
Myrcene	0.59	0.39	0.35
Limonene	0.82	0.53	0.49
γ-Terpinene	0.15	0.10	0.09
p-Cymene	0.41	0.27	0.24
1-Methyl-4-isopropenyl benzene	0.08	0.05	0.05
α-Cedrene	0.18	0.12	0.10
Unknown sesquiterpene	1.28	0.83	0.76
β-Caryophyllene	0.32	0.21	0.20
β-Elemene	0.23	0.15	0.14
α-Farnesene	0.13	0.08	0.08
δ-Cadinene	0.85	0.56	0.50
Unknown sesquiterpene	0.07	0.05	0.04
β-Selinene	1.14	0.75	0.68
Unknown sesquiterpene	0.25	0.14	0.13
Unknown sesquiterpene	0.58	0.38	0.34
β-Bisabolene	0.10	0.07	0.06
cis-Chrysanthenyl acetate	58.50	61.30	52.30
Bornyl acetate and chrysanthenone	3.00	4.20	0.60
Citronellyl acetate	13.40	10.70	25.30
Mixture of an ester and a hydroxy compound	15.20	15.70	15.00
Unrecovered material	1.30	2.50	1.00

*Resolved and identified by GLC/MS.

Discussion

The percentage yield of the essential oil from the immature seeds of Nushki is much higher as compared to the ones of the mature seeds of Nushki and Quetta. As

expected, all the three oils have similar physico-chemical values. The ester value of the oils is rather high, indicating the presence of a large amount of esters. This is further supported by IR of the three oils, which showed strong peaks at 5.8 and 8.1 nm due to carbonylic and ester groups.

The first oxygenated component of the oil as eluted with 2% diethyl ether in n-hexane was a single compound. It was an ester by IR: (3.1, 3.5, 6.9, 7.4, 7.9, 8.25, 8.5, 9.4, 9.7, 10.2, 10.6, 12.8 nm). The NMR of the compound was (DMSO^{d6}): τ 9.14 (S, 3H, $C\underline{H}_3$), τ 8.5 (S, 3H, $C\underline{H}_3$), τ 8.4 (m, 3H, $C\underline{H}_3$), τ 8.14 (m, 2H, $C\underline{H}_2$), τ 7.8 (m, 2H, $C\underline{H}_2$), τ 6.7 (m, 2H, $C\underline{H}_2$), τ 6.2 (S, 1H, O$\underline{H}$), τ 4.8 (m, 1H, vinylic-$\underline{H}$). From these data the compound was identified as *cis*-chrysanthenyl acetate.[3] Attempted hydrolysis of the above ester gave an unsaturated aldehyde identified as 1-formyl 2,2,4-trimethyl-cyclohex-3-ene, IR: (3.4, 3.7, 5.8, 6.9, 7.3 nm) and 2,4-dinitrophenyl hydrazone, m.p. 155-156° (lit[4], m.p. 150-151°).

The second fraction contained a mixture of two compounds. One compound was an ester while the other a ketone. The ester was identified as bornyl acetate by IR comparison with its authentic sample and the ketonic compound was found to be chrysanthenone.

Further elution of the column gave a mixture of two compounds by TLC. One of the compounds was a crystalline solid and the other an ester. The ester was identified as citronellyl acetate by TLC, IR and GLC comparison.

The next fraction was eluted from the column with 10% diethyl ether in n-hexane. On hydrolysis with 0.5N alcoholic potassium hydroxide, it gave a mixture of two compounds by TLC whose IR showed hydroxy and carboxylic absorption. It could be an ester of α-pinene skeleton in which the four membered ring ruptured during hydrolysis.

Finally the column was eluted with 50% diethyl ether in n-hexane which gave a mixture of two compounds. The mixture consisted of an ester and a hydroxy compound by TLC and IR.

A noteworthy feature of the chemical composition of the essential oil of the *Ducrosia anethifolia* is that the occurrence of *cis*-chrysanthenyl acetate in the *Umbelliferae* species is quite novel. The yield of the oil is relatively high and the material obtained by steam distillation is typical because of its sharp note. The immature seed seems to have higher content of the oil. The essential oil may find reasonably good place in cosmetics and perfumery. Our successful cultivation of the species in PCSIR Laboratories, Lahore, will, therefore, prove valuable.

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