Pak J Sci Ind Res 1999 42 (4) 188-191

Chemical Composition of *Thuja orientalis* L. Fruits at Different Stages of Maturity

M Riaz*, Shadab Qamar, M Rashid and F M Chaudhary

Applied Chemistry Research Centre, PCSIR Laboratories Complex, Lahore-54600, Pakistan

(Received 22 October 1996; accepted 27 June 1998)

The essential oil obtained by hydrodistillation of the fruits from *Thuja orientalis* at two stages was analysed by GC and GC/MS. Among the compounds indentified, α-pinene (41.48-45.61%), Δ^3-carene (32.69-34.55) β-terpinene (2.28-2.51%), ρ-cymene (1.29-2.23%), cedrol (1.82-4.50%), camphene (1.78-1.96%), D-limonene (1.47.2.40%) and myrtenol (1.27-4.40%) were found to predominate, while other compounds were either in small quantities (i.e. less than 1%) or in traces.

Key words: *Thuja orientalis* L., Coniferae, Monoterpenes, Sesquiterpenes.

Introduction

Thuja orientalis L., N.O. Confierae (Kirtikar and Basu 1933) is locally known as "More punkh". It is grown in the gardens as an ornamental plant. The plant finds applications as hemostatics (Kosuge *et al* 1985a) and cytotoxic (Kosuge *et al* 1985b) in the Chinese system of medicine.

Although considerable investigations have been carried out (Vashist *et al* 1963; Sakhatov and Belova 1967; Tomita and Hirose 1968; Traud and Musche 1983) on the chemical composition of the oil from leaves, wood and cones, yet the oil from Pakistan does not appear to have been studied earlier.

In continuation of our screening programme of Pakistani aromatic flora (Riaz and Chaudhry 1990; Riaz *et al* 1989, 1994, 1995), the physico-chemical characteristics (Table 1) and chemical composition of the oil (Table 2) are reproted here.

Materials and Methods

Fruits of *Thuja orientalis* L., were collected from the premises of PCSIR Laboratories Complex, Lahore at two stages (raw and ripe) in the months of March and September. The fruits (344g and 500g respectively) were subjected to simultaneous distillation and solvent extraction using Likens and Nickerson apparatus(Likens and Nickerson 1964) for 10-15 h until there was no significant increase in the volume of the oil collected. The oils were then dried (using anhydrous sodium sulphate), filtered and weighed. The yields were 0.28% from the fruits collected in March and 0.14% from those collected in September on wet basis.

*Author for correspondence

Physico-chemical parameters such as specific gravity, refractive index (Abbe's), acid and ester numbers were measured according to the standard procedure (Guenther 1948)and are given in Table 1.

Identification by GC and GC/MC : Gas chromatographic analyses were conducted on a Schimadzu GC-14 chromatograph equipped with a flame ionization detector, fitted with 25 m x 0.22 mm (i.d.) WCOT SE-30 fused silica column. Nitrogen was used as a carrier gas with a flow velocity of 1-2 ml min^{-1} and split ratio 1:100 and sample size 0.2 µl. The column temperature was programmed at 60°C for 0 min with 4°C min^{-1} rise to 200°C while detector and temperatures of 300°C and 250°C respectively were used. Percentage composition of each component was calculated on the basis of peak area using a Schimadzu C-R4A chromatopac electronic integrator.

Jeol Model JMS-A x 505 H mass spectrometer combined with Hewlett Packard 5890 series gas chromatograph, was used for GC/MS analysis. Oil samples were injected on a 25 m x 0.22 WCOT BPS (5% phenyl, 95% dimethyl siloxane)

Table 1

Physico-chemical characteristics of oil at two stages

	Raw	Ripe
Percentage of essential oil on wet basis	0.28	0.14
Wt (gm ml^{-1}) of the oil at 30°C	0.8861	0.8835
Refactive index at 30°C	1.4730	1.4740
Acid value (mg KOH g^{-1} oil)	0.38	1.35
Ester value (mg KOH g^{-1} oil)	14.81	15.05

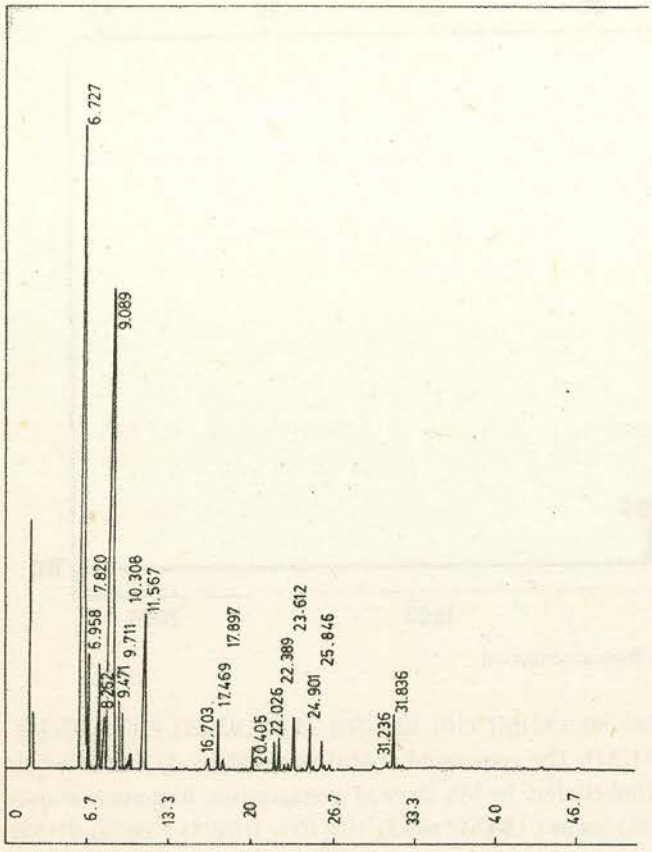

Fig 1. GC of *Thuja orientalis* fruits essential oil (RAW).

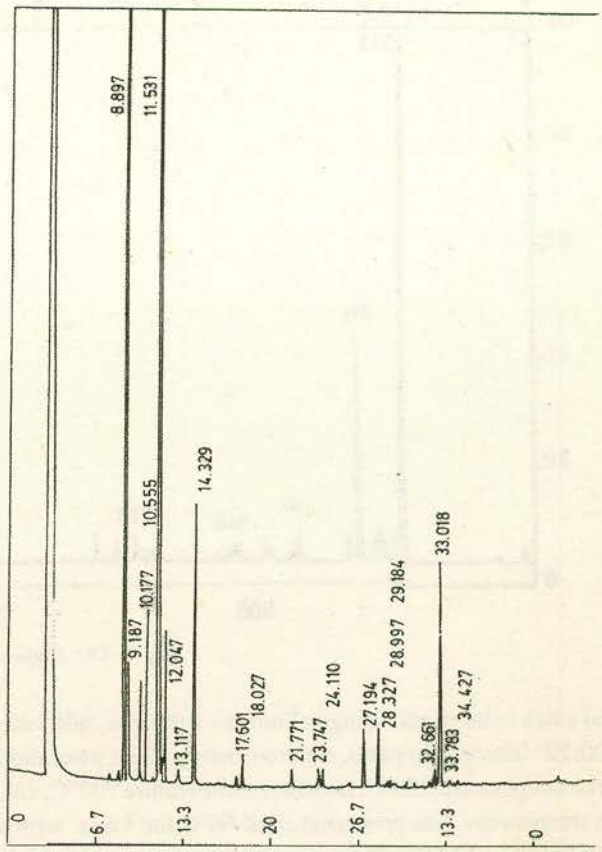

Fig 2. GC of *Thuja orientals* fruits essential oil (Ripe).

Table 2

Composition of essential oils (%)[c] in fruits of *Thuja orientalis* at different stages of maturity

Peak[d]	Rt (Seconds)	Compound	Raw	Ripe	Mass Fragmentation[e&f]
1.	238	α-pinene	41.48	45.61	93,41,49,121,136,105
2.	250	camphene	1.78	1.96	93,79,121,136,107,49
3.	273	ρ-cymene	2.23	1.29	119,91,134,77,65,39
4.	280	β-terpinene	2.51	2.28	93,69,41,75,136,141
6.	320	Δ^3-carene	34.55	32.69	93,77,71,136,121,41
6(a)	333	β-cymene	traces	traces	139,134,93,91,77,41
7	338	*D*-limonene	1.47	2.04	68,93,136,79,121,107
8.	430	α-campholenal	0.83	0.27	108,93,95,67,41,83
10(a)	485	umbellulol	traces	traces	91,119,134,41,70,55
15.	564	myrtenol	1.27	4.40	79,91,119,108,41,134
16(a)	600	umbellulon	0.43	0.31	108,107,135,150,91,79
16(b)	642	(Z)-cinerone	traces	traces	150,107,135,32,91,67
17.	685	1-α-bornylacetate	0.49	0.31	95,136,121,43,108,80
19.	700	verbenene	traces	traces	91,43,107,135,77,65
26.	1089	α-longipinene	traces	traces	119,161,204,93,101,69
27.	1104	cedrol	1.82	4.50	119,161,93,69,105

c) Percentages calculated from the peak area in GC. d) Peak number given in order of appearence in total ion chromatogram.
e) Main fragments in decreasing order of peak intensity. f) Molecular weight of the fragment over charge on the ion.

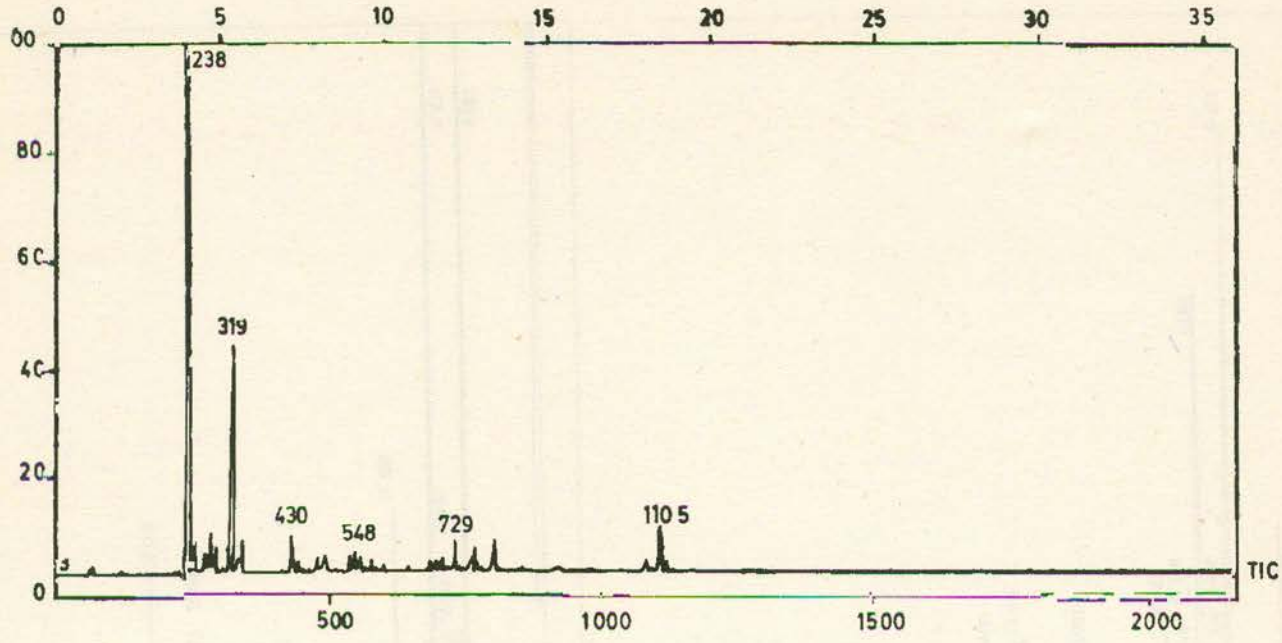

Fig 3. TIC *Thuja orientals* fruits essential oil.

fused silica column and using helium as carrier gas, split ratio 1:100, EI⁺ (electron impact), electron energy 70 ev, ionization source temperature 250°C, interface temperature 230°C, column temperature was programmed at 60°C for 4 min with a 6°C min^{-1} rise to 220°C. Data acquisition and processing were performed by Jeol JMA-DA 5000 system with library search system. Various components were identified by their retention time and MS library search.

Results and Discussion

The essential oil obtained by hydrodistillation of the raw and ripe fruits of *T.orientalis* L. was analysed by GC/MS (Figs 1-3). Its composition given in Table 2 is quite similar to the composition of essential oil of the leaves and fruits of *C.sempervirens* L., which contains large amounts of α-pinene (41 .48-45.65%) and Δ^3–carene (32.69-34.55%).

A review of Table 2 indicates that the percentage of α-pinene, myrtenol and cedrol increased with the maturity of the cones, while in contrast the percentage of Δ^3-carene, ρ-cymene and α-campholenal decreased with the maturity of cones.

GC and GC/MS analysis of the oil afforded 28 and 36 well resolved components, of which 16 were identified. The chemical constituents identified consist of seven monoterpene hydrocarbons (84.02-85.87%),sevenoxygenated monoterpenes (3.02-5.02%), one sesquiterpene and one oxygenated sesquiterpene.

The constituent of peak 8 was tentatively identified as α-campholenal. Its MS showed important peaks at m/z (%) (ret.int): 152 $[M]^+$ (10), 108(100), 93(55), 93(55), 91(39), 67(31), 41(31). The compound at 6(a) was tentatively identified as Umbellulon. Its MS showed characteristic fragments at m/z (%) (ret.int), 150$[M]^+$ (68.2), 108(100), 107(98), 135(79), 91(55) and 79(37), in accordance with the expected fragments of this structure (Adams 1995). The component at peak 16(b) was tentatively identified as Z-cinerone. Its MS showed important peaks at m/z (%) (ret.int.) 150 $[M]^+$ (100), 135(60), 107(60), 91(42), 32(43) and 67(31).

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