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COMPOSITION OF THE ESSENTIAL OILS OF *Thymus* SPECIES GROWING IN TURKEY

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All the *Thymus* species growing in Turkey are aromatic plants which are often used as herbal tea, condiments and folk medicine.

The origin of the genus *Thymus* is assumed to lie in Southern Europe, showing two different centers, i.e., the Iberian Peninsula together with North West Africa and the Balkan peninsula.

At the same time, the high variability in shape and form of the genus *Thymus* has always confronted the taxonomist with the problem of dividing the genus into clearly defined species and caused them to increase in number [1].

For the genus *Thymus*, Karl Ronniger regards 417 binary names as acceptable: whereas, Jalas estimates the number of *Thymus* species at 150 (38 of which are located in Turkey, the 38th species has recently been found by our group). Thirty-eight species are represented by 64 taxa and 24 of which are endemic [2].

While the early studies on *Thymus* essential oils started between 1946 and 1948 in Turkey, the first significant study was carried out in 1973 [3-8]. A detailed study has been carried out by the TBAM group since 1990 covering all the *Thymus* species growing in Turkey [9-23].

The results of chemical analysis of essential oils in *Thymus* species and of the clarification of chemotypes observed among these species will be given here.

The essential oils from 91 samples representing 34 out of 64 taxa existing in Turkey have been analyzed by our group.

Collection of samples from different geographical locations and populations enabled us to identify chemotypes within or outside the same population of the said *Thymus* taxon.

Thymus is an important genus due to presence in the oils of high concentration of carvacrol and thymol which are isomeric phenolic terpenes. However, there are *Thymus* species poor in phenolic compounds and some do not contain phenolic compounds at all. During our study, we have come across all three types.

Dried herbal parts of *Thymus* species are used as spice and herbal tea in Turkey. However, they are not used in the production of thyme oil. In Turkey, other carvacrol or thymol-rich genera such as *Origanum*, *Thymbra*, *Coridothymus*, and *Satureja* are used for essential oil production instead of *Thymus*.

Phenol-rich *Thymus* species are used in diabetes, stomach and intestinal diseases, for cough as herbal tea and also as condiment; whereas, phenol-poor or phenol-less *Thymus* species are used, due to their pleasant aroma, as herbal tea, where they grow.

Among the papers published between 1960 and 1989, Stahl-Biskup recently reviewed all the studies on the essential oils of *Thymus* species. Her compilation covers 140 studies on 80 taxa.

She reported that 33 compounds in the oils with amounts 5% or more were characteristic for Thyme oil.

We hereby give the results of 91 analyses carried out in our laboratories on 34 taxa collected from different localities (Table 1). We have proved that 28 compounds with more than 2% make up the main constituents of Thyme oils.

Stahl-Biskup has classified *Thymus* oils according to three terpene groups.

The first group comprises nine terpenes which are found in many different species in remarkably high concentrations. These are thymol, carvacrol, linalool, linalyl acetate, borneol, p-cymene, 1,8 cineole, γ-terpinene and camphor.

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TABLE 1. Major Components of the Essential Oils of *Thymus* Species Native to Turkey. Our Results

Name	End*	Locality (No. collection)	Yield %	Main components %
T. argaeus	E	Eskişehir (3)	0.8-1.3	linalyl acetate 45-66, linalool 10-15
T. atticus		Tekirdağ	0.2	caryophyllene oxide + terpinen-4-ol 14
T. atticus		Edirne	0.6	thymol 38, *p*-cymene 10
T. bornmuelleri	E	Bursa	0.7	thymol 45, *p*-cymene 13
T. cariensis	E	Muğla (2)	0.2-0.4	borneol 13-19, 1,8-cineole 10-13, α-pinene 12, camphor 8-9
T. cilicicus	E	İçel	1.5	α-pinene 17, 1,8-cineole 10
T. comptus		Tekirdağ	0.8	thymol 36
T. comptus		Kirklareli	1.0	thymol 50
T. eigii		Adana (2)	0.2-1.8	carvacrol 30-65
T. haussknechtii	E	Elaziğ (2)	0.05-0.5	linalool 5-20, caryophyllene oxide 7-12, borneol 10-11
T. kotschyanus var. *eriophorus*		Ağri	0.9	carvacrol 28, thymol 18, *p*-cymene 15
T. kotschyanus var. *glabrescens*		Adiyaman	0.5	thymol 45, p-cymene 18
T. kotschyanus var. *glabrescens*		Kahraman Maraş	1.9	carvacrol 53
T. kotschyanus var. *kotschyanus*		Malatya	1.9	carvacrol 60
T. leucostomus var. *argillaceus*	E	Eskişehir (4)	0.6-1.0	thymol 16-35, carvacrol 15-26, borneol 12-24, *p*-cymene 11-15
T. leucostomus var. *leucostomus*	E	Eskişehir	0.5	carvacrol 22, *p*-cymene 18, thymol 14
T. longicaulis ssp. *chaubardii* var. alternatus		Kütahya	3.4	thymol 70
T. longicaulis ssp. *chaubardii* var. *chaubardii*		Kütahya (2)	2.1-3.4	thymol 65-67
T. longicaulis ssp. *chaubardii* var. *chaubardii*		Balikesir	1.2	thymol 45, *p*-cymene 14
T. longicaulis ssp. *chaubardii* var. *chaubardii*		Bursa	0.6	carvacrol 42, thymol 19
T. longicaulis ssp. *chaubardii* var. *chaubardii*		Eskişehir	0.05	linalool 35, carvacrol 18, thymol 12
T. longicaulis ssp. *longicaulis* var. *longicaulis*		Kütahya	1.7	α-terpinyl acetate 82
T. longicaulis ssp. *longicaulis* var. *longicaulis*		Kütahya	0.8	geraniol 69, geranyl acetate 16
T. longicaulis ssp. *longicaulis* var. *longicaulis*		Kütahya	0.3	thymol 53, *p*-cymene 18

Name	End*	Locality (No. collection)	Yield %	Main components %
T. longicaulis ssp. *longicaulis* var. *subisophyllus*		Balikesir (11)	0.1-2.1	thymol 21-57
T. longicaulis ssp. *longicaulis* var. *subisophyllus*		Burdur	1.7	thymol 26, carvacrol 26, γ-terpinene 14
T. longicaulis ssp. *longicaulis* var. *subisophyllus*		Denizli	1.7	thymol 56
T. longicaulis ssp. *longicaulis* var. *subisophyllus*		Tekirdağ	1.3	thymol 57
T. longicaulis ssp. *longicaulis* var. *subisophyllus*		İzmir	3.2	thymol 58, *p*-cymene 12
T. longicaulis ssp. *longicaulis* var. *subisophyllus*		Eskişehir	2.1	linalyl acetate 63, linalool 11
T. pectinatus var. *pectinatus*	E	Eskişehir (3)	0.2	thymol 13-35, *p*-cymene 11-33, borneol 10-18
T. praecox ssp. *grossheimii* var. *grossheimii*		Trabzon	0.3	carvacrol 19, *p*-cymene 10
T. praecox ssp. *grossheimii* var. *grossheimii*		Trabzon	0.7	thymol 25, *p*-cymene 23
T. praecox ssp. *skorpilii* var. *laniger*	E	Amasya	0.1	thymol 18, carvacrol + eudesmol 13
T. praecox ssp. *skorpilii* var. *laniger*	E	Bursa	0.8	thymol 41
T. praecox ssp. *skorpilii* var. *skorpilii*		Sinop	0.5	α-terpineol+ α-terpinylacetate 25, geraniol 24
T. pseudopulegioides		Trabzon	0.6	linalool 26, α-terpinyl acetate 15
T. pulvinatus	E	Balikesir (2)	0.4-0.9	borneol 29-31
T. revolutus	E	Antalya	0.3	*p*-cymene 39, borneol 12
T. roegneri		Balikesir	1.0	thymol 54, *p*-cymene 17
T. sibthorpii		Balikesir (3)	0.8-1.7	thymol 24-50, *p*-cymene 17-18
T. sibthorpii		Balikesir	1.8	carvacrol 39, *p*-cymene 17
T. sibthorpii		Kirklareli	1.5	carvacrol 40, *p*-cymene 22, thymol 16
T. sibthorpii		İzmir	0.8	thymol 38, *p*-cymene 28
T. sipyleus ssp. *rosulans*		Afyon	1.2	thymol 68
T. sipyleus ssp. *rosulans*		Ankara	0.9	thymol 68
T. sipyleus ssp. *rosulans*		Bursa	0.5	thymol 17, carvacrol 12
T. sipyleus ssp. *rosulans*		Ankara	0.7	thymol 39, carvacrol 20
T.sipyleus ssp. *rosulans*		Zonguldak	0.2	1,8-cineole 20

Name	End*	Locality (No. collection)	Yield %	Main components %
T. sipyleus ssp. *sipyleus* var. *sipyleus*	E	Muğla	0.1	geranial 26, neral 14
T. sipyleus ssp. *sipyleus* var. *sipyleus*	E	Ankara	0.2	geranial 29, neral 21
T. sipyleus ssp. *sipyleus* var. *sipyleus*	E	Denizli	0.3	linalool 22, geranial 8, neral 3
T. striatus var. *interruptus*		Kirklareli	0.1	β-caryophyllene + terpinen-4-ol 27
T. striatus var. *interruptus*		Kirklareli	0.4	p-cymene 15, 1,8-cineole 13, thymol 11
T. striatus var. *interruptus*		Kirklareli (2)	1.3	thymol 36
T. syriacus		Gaziantep	0.7	thymol 50, carvacrol 16
T. thracicus var. *longidens*		Balikesir (2)	1.2-1.3	geraniol 16-47
T. transcaucasicus		Artvin	0.1	germacrene D 32, -caryophyllene 18
T. zygioides var. *lycaonicus*	E	Tekirdağ	0.9	thymol 45, β-bisabolene 11
T. zygoides var. *lycaonicus*	E	Uşak	1.1	thymol 58, *p*-cymene 11
T. zygoides var. *lycaonicus*	E	Kirklareli	1.1	thymol 50
T. zygoides var. *lycaonicus*	E	Manisa (2)	1.1	carvacrol 62
T. zygoides var. *lycaonicus*	E	Manisa	0.2	geraniol 77
T. vulgaris	C	Adana	1.0	thymol 36, *p*-cymene 30

*E: Endemic, C: Cultivated

Author names have been omitted. Accepted names in the Flora of Turkey (P. H. Davis (ed.), Flora of Turkey and the East Aegean Islands, Vols. 1-10, Univ. Press Edinburgh, 1965-88) are used in this paper

The second group is found only in a few species but when they are found they are present in relatively high concentrations. These are geranyl acetate, α-terpineol, α-terpinyl acetate, dihydrocarvon, citronellol, geranyl butyrate, hedicaryol and carvon.

The third group comprises compounds that are typical minor components in *Thymus* essential oils. These are terpinen-4-ol, β-caryophyllene, geraniol, bornyl acetate, trans-sabinene hydrate, α-humulene, caryophyllene epoxide, β-bisabolene, 1-octen-3-ol, neryl acetate, nerolidol, carvacrol methyl ether, thymol methyl ether, germacrene D and β-terpineol.

As compared with our studies, conclusions for the first and second groups are valid for the Turkish *Thymus* essential oils as 80% of the Thyme oils fall into the first group.

Of the compounds belonging to the second group, α-terpineol + α-terpinyl acetate (25.06%) are the main components of the oil of *Thymus praecox* ssp. *skorpilii* var. *skorpilii*.

α-terpinyl acetate (82.07%) is the main compound of the oil of *Thymus longicaulis* ssp. *longicaulis* var. *longicaulis*.

Although the compounds listed in group 3 are regarded as minor components, geraniol was found to be the major compound in the following two thyme oils.

Geraniol: 69% in *Thymus longicaulis* ssp. *longicaulis* var. *longicaulis*.
47% in *Thymus thracicus* var. *longidens*.

β-caryophyllene + terpinen-4-ol were found to be the major components (27%) in the oil of *Thymus striatus* var. *interruptus*.

Except for these, there are some other compounds which did not appear in Stahl-Biskup's list;

Geranial/Neral = Citral is the major component of *Thymus sipyleus* ssp. *sipyleus* var. *sipyleus* collected from two different localities (MuÛla and Ankara) at 39% and 50%, respectively. These results suggest that *Thymus* species growing in Turkey do not fit thoroughly with her classification.

Thirty-four species studied by us showed different chemotypes. Ten in different populations and two in the same population.

We detected three chemotypes of *Thymus longicaulis* subsp. *longicaulis* var. *longicaulis* growing side by side in a population covering an area of 1 square meter. Each of these chemotypes smelled like thyme, rose and lavender. The oils contained thymol (53%), geraniol (69%) and α-terpinyl acetate (82%) as major components, respectively.

In official *Thymus* species, thymol content is desired to be between 20 and 45 percent (Ph. Helvetica). Such plants are not regarded as sources of thymol but their extracts or oils are used in some preparations.

Twenty Thyme species with high thymol-content have been studied by us. This means that in 59% of the 34 taxa studied, thymol is the major component in the oils.

Two varieties of *Thymus longicaulis* subsp. *chaubardii* were found to be the richest in thymol content, namely var. *alternatus* (70%) and var. *chaubardii* (67%).

There are nine Thyme species containing carvacrol as the major constituent. The highest carvacrol content hitherto encountered in Turkish Thyme species was found in the oil of *Thymus eigii* (65%).

On the other hand, there are 16 species which contain other compounds than thymol/carvacrol as main constituents. Ten of these are chemotypes.

To summarize our results;

– Thymol is the main compound in most *Thymus* species growing in Turkey. Of these, 15 species may be regarded as official, since thymol content in them falls between the accepted limits.

– As is the case in other countries, chemotypes have been found among the *Thymus* species of Turkey.

– The theory of the effect of "Environmental Factors and Ecologic Interactions" on the evolution of chemotypes is not valid also for the known chemotypes of *Thymus* species growing in Turkey.

EXPERIMENTAL

Plant Material

All *Thymus* samples were collected from different localities. These are the plant materials which have been used in this study. Voucher specimens are kept at the Herbarium of the Faculty of Pharmacy (ESSE), Anadolu University, Eskişehir, Turkey.

Distillation

Plant materials were hydrodistilled for 3 h using a Clevenger-type apparatus.

GC Analysis

The GC analysis was carried out on a Shimadzu GC-9A with CR-4A integrator. Thermon-600T fused silica capillary column (50 × 0.25 mm) was used. Carrier gas was nitrogen. Oven temp. was kept at 70°C for 10 min and programmed to 180°C at a rate of 2°C/min, then kept at 180°C for 30 min. Injector and detector (FID) temperatures were 250°C.

GC/MS Analysis

The GC/MS analysis was carried out with Shimadzu GC/MS QP2000A system. Thermon-600T fused silica capillary column was used with helium as carrier gas. MS were taken at 70 eV. Scanning speed was scans/sec. from m/z 10 to 400.

Library search was carried out using LSS-30 Library Search Software from the NBS/NIH/EPA Library, the Wiley/NBS Registry Mass Spectral Data, TBAM Library of Essential Oil Constituents, comparison with reference compounds and retention indices in published sources [24-26].

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