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CARVACROL-RICH PLANTS IN TURKEY

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Carvacrol is a phenolic monoterpene isomeric with thymol. While thymol is crystalline, carvacrol is a liquid with thymol-like characteristic odor. It is practically insoluble in water but freely soluble in ethanol and ether. It is the major constituent in the essential oils of plants known and used as "Kekik" in Turkey (oregano in Greece) [1-4]. In Turkey, such plants are used as condiment to impart a spicy flavor to food or as herbal tea. The carvacrol-rich oils are externally used by rubbing on skin to sooth rheumatic pain [5, 6]. Scientific evidence for such a use has recently appeared in the world literature, when carvacrol was found to inhibit prostaglandin-synthesis which is an important mechanism in pain-killing and anti-inflammatory processes [7]. The distillates of *Origanum*, *Satureja*, etc., after the oil is removed, are taken orally to cure stomach ulcers [8].

Other reported biological effects of carvacrol are as follows: antibacterial [9, 10], antifungal [11-13], antispasmodic [14, 15], acetylcholine esterase inhibition [16], lipid peroxidase inhibition [17], radical scavenging effect [17], white blood cell macrophage stimulant [18], and cardiac depressant activity [19]. Due to their antioxidant properties carvacrol-rich oils are recommended for the preservation of food [17, 20, 21].

Carvacrol has been reported to be a constituent in the essential oils not only of Labiatae but also of other families such as Chenopodiaceae, Plantaginaceae, Umbelliferae, Verbenaceae, etc. Carvacrol-rich oils reported earlier from Labiatae are as follows: *Lavandula multifida* (47-86%) [22], *Coridothymus capitatus* (86%) [23], *Origanum syriacum* (83%) [24], *Origanum dictamnus* (59-82%) [25], *Origanum onites* (51-81%) [26], *Thymus eigii* (75%) [27], *Origanum majorana* (48-74%) [28]. Non-Labiatae oils in which carvacrol is the major constituent are the following: *Anabasis setifera* (Chenopodiaceae) (85%) [29], *Carum carvi* (Umbelliferae) (60%) [30], *Lippia graveolens* (Verbenaceae) (25%) [31], *Lippia sidoides* (Verbenaceae) (25%) [32], *Plantago asiatica* (Plantaginaceae) (18%) [33].

Extensive research into essential oil bearing plants of Turkey ongoing for the last seven years by our group has shown that carvacrol-rich plants in Turkey belong to the family Labiatae. As mentioned earlier, carvacrol-rich plants are indiscriminately known as "Kekik" due to their thyme-like odor. Such plants include several species of the genera *Origanum*, *Satureja*, *Thymbra*, *Thymus*, and *Coridothymus capitatus*. These plants are collected from the wild and either used locally or exported after drying. *Satureja hortensis* is cultivated for use in fresh form as a spice plant. It is also a native plant of Turkey. In recent years, some companies have started the cultivation of *Origanum onites* near İzmir in the Aegean Region of Turkey.

Table 1 gives a list of carvacrol-rich plants of Turkey in alphabetical order.

The essential oils of *Origanum* species are rich in carvacrol and all of these species are of commercial importance [1, 2]. Twenty-nine samples of *Origanum vulgare* subsp. *hirtum* collected from eight different regions have shown that the oils contained 44-85% carvacrol [34]. In the oils of six *Origanum majorana* (=*O. dubium*) samples collected from two regions, carvacrol content was found as 38-88% [35]. Twenty-four samples of *Origanum onites* from ten regions had 19-82% carvacrol in their oils [1, 2], while six samples of *Origanum minutiflorum*, an endemic species for Turkey, collected from two regions contained 42-84% carvacrol in the oils. Finally, 43-79% carvacrol was observed in the oil of *O. syriacum* var. *bevanii* collected from three regions [37]. These five Origanums make up the majority of kekiks exported from Turkey. According to 1993 figures, 5500 tonnes were exported for a return of 13.3 million dollars, unit export value was $2.43 per kg [2].

Another carvacrol-rich genus is *Thymbra*, which is represented by two species and four taxa in Turkey. Three out of four of these taxa have been studied by our group. The results are tabulated in Table 1. The oils of sixteen *Thymbra spicata*

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TABLE 1. Carvacrol-rich Plants in Turkey

	End	Region	Oil Yield %	Carvacrol %	Ref.
Coridothymus capitatus	–	Muğla Çanakkale Balikesir	2.0 0.5 2.7	69 78 71	40
Melissa officinalis subsp. *altissima*	–	Balikesir	0.02	60	*
Origanum onites	–	Antalya (2 samples) İzmir (11 samples) İçel Balikesir (2 samples) Yozgat Manisa Aydin Adana (2 samples) Muğla (2 samples) Denizli	2.3-3.1 0.6-2.8 7.7 1.9 0.1 3.0 2.9 2.1-2.8 2.5-3.9 4.8	50-82 55-80 78 73-77 74 71 70 19-70 67-77 78	1, 2
Origanum bilgeri	E	Antalya	3.0	66	*
Origanum hypericifolium	E	Burdur Antalya	2.5 0.9	64 34	*
Origanum majorana	–	Antalya (5 samples) İçel	1.3-6.5 7.7	38-88 75	1, 2
Origanum minutiflorum	E	Isparta (5 samples) Antalya	2.4-2.5 1.1-2.5	42-84 56-77	1, 2
Origanum munzurense	E	Tunceli	0.2	51	*
Origanum syriacum var. *bevanii*	–	Adana Hatay Kahramanmaraş	0.4 3.8 3.7	79 55 43	37
Origanum vulgare subsp. *vulgare*	–	Çanakkale Erzincan	3.6 0.6	37 26	1
Origanum vulgare subsp. *hirtum*	–	İçel (2 samples) Balikesir (14 samples) Çanakkale (3 samples) Bursa (5 samples) İzmir Aydin (2 samples) Manisa Muğla	2.2-5.7 2.6-6.5 1.3-3.6 1.6-3.5 1.5 2.5-3.9 1.9 3.0	66-85 44-79 67-77 56-75 71 69-70 64 58	34
Satureja cilicica	E	İçel Kahramanmaraş	0.6 0.9	21 38	*
Satureja cuneifolia	–	İçel Eskişehir (2 samples) Balikesir (2 samples) İzmir (3 samples) Muğla	0.3 0.7 2.7 0.6-1.5 0.6	26 38-19 47-53 58-69 72	*
Satureja hortensis	–	Adana (3 samples) Edirne (2 samples) Eskişehir Balikesir (4 samples) Konya	1.9-3.2 2.2-2.3 1.9 1.7-2.7 2.5	47-57 47-48 50 52-55 63	*
Satureja montana	C	Adana (3 samples)	0.03-2.8	53-63	*
Satureja parnasica subsp. *sipylea*	E	Balikesir (3 samples)	1.5-2.0	43-47	*

Species	End	Region	Oil Yield %	Carvacrol %	Ref.
Satureja spicigera	–	Trabzon	0.5	26	*
Satureja thymbra	–	Muğla (3 samples) Antalya (2 samples) Aydin	1.0-4.3 2.9-3.7 2.8	30-45 41-47 49	*
Stachys cretica subsp. *anatolica*	–	Balikesir	0.09	33	*
Thymbra sintenisii subsp. *isaurica*	E	Antalya	1.6	39	*
Thymbra spicata var. *spicata*	–	Muğla Bilecik Eskişehir Balikesir (2 samples) Kirklareli K. Maraş (2 samples) Gaziantep (4 samples) Antalya (4 samples)	0.7 2.2 3.0 1.1-1.8 1.0 2.4-3.4 0.8-2.3 0.5-5.2	56 58 64 64 65 61-66 59-72 56-77	38
Thymbra spicata var. *intricata*	E	Adana Antalya (2 samples) Tekirdağ İçel Muğla (2 samples)	1.7 0.3-2.0 2.0 2.7 1.4-2.4	55 49-60 66 71 66-71	38
Thymus eigii	–	Adana (2 samples)	0.2-1.8	30-65	39
Thymus kotschyanus var. *eriophorus*	–	Ağri	0.9	28	39
Thymus kotschyanus var. *glabrascens*	–	Kahramanmaraş	1.9	53	39
Thymus kotschyanus var. *kotschyanus*	–	Malatya	1.9	60	39
Thymus leucostomus var. *argillaceus*	–	Eskişehir (4 samples)	0.6-1.0	15-26	39
Thymus leucostomus var. *leucostomus*	–	Eskişehir	0.5	22	39
Thymus longicaulis subsp. *longicaulis* var. *subisophyllus*	–	Balikesir	0.6	32	39
Thymus longicaulis subsp. *chaubardii* var. *chaubardii*	–	Bursa	0.6	42	39
Thymus praecox ssp. *grossheimii* var. *grossheimii*	–	Trabzon	0.3	19	39
Thymus sibthorpii	–	Kirklareli Balikesir	1.5 1.8	40 39	39
Thymus zygoides var. *lycaonicus*	E	Manisa	1.0	62	39
Gentiana lutea subsp. *symphyandra* (Gentianaceae)	–	Kütahya	0.001	23	*

*: Unpublished results of TBAM.
E: Endemic.
C: Cultivated.

var. *spicata* samples collected from eight regions contained carvacrol (59-77%) as the major constituent. The other endemic variety of this species, var. *intricata*, has a limited distribution in the Southern part of Turkey. This plant is also used as an aromatic herb. In the oils of seven samples collected from five different localities carvacrol content ranged from 50-71% [38]. Another endemic species, *T. sintenisii* subsp. *isaurica* contained 39% carvacrol in the oil obtained in 1.6% yield.

Eleven *Thymus* taxa out of 64 taxa known to occur in Turkey were found to contain carvacrol (8-65%) as major constituent in their respective essential oils [39].

Satureja species are widely used as condiment (in fresh and dried form), folk medicine, and as a source of essential oil. Some (e.g., *S. hortensis*) are cultivated but most are collected from the wild. *Satureja* is represented in Turkey by 14 species plus *S. montana* which is introduced to Turkey for cultivation. We have found carvacrol (19-69%) as the major constituent in the oils of seven species (35 samples collected from 18 regions).

Coridothymus capitatus is a monotypic genus widely distributed in the mediterranean region. The oils from three collections showed carvacrol (69-78%) as the major component [40].

The above mentioned species, belonging to the family Labiatae, can be regarded as carvacrol-rich since, with only a few exceptions, they all contain carvacrol as the main constituents in their essential oils. Due to similar odor characteristics, all of these carvacrol-rich species are considered thyme-like or oregano-like and are invariably called "Kekik."

However, we have come across some other species, during our studies, which also contained carvacrol as the main constituent in their oils. Carvacrol cannot be regarded as a characteristic major constituent in the oils of these genera. They are as follows:

Melissa officinalis subsp. *altissima* (Labiatae) (60% in herb oil).

Stachys cretica subsp. *anatolica* (Labiatae) (33% in herb oil).

Gentiana lutea subsp. *symphyandra* (Gentianaceae) (23% in root oil).

EXPERIMENTAL

The plant materials subjected to this study and their essential oil contents are listed in Table 1. Voucher specimens are kept at the Herbarium of the Faculty of Pharmacy (ESSE), Anadolu University, Eskişehir, Turkey. Plant materials were hydrodistilled for 3 h using a Clevenger-type apparatus. The GC analysis was carried out using 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. The GC/MS analysis was carried out with the 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 2 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 [41-43].

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