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Farklı Kurutma Yöntemlerinin Kekik (*Thymus sipyleus* Boiss. var. sipyleus) Uçucu Bileşenleri Üzerine Etkisi

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Öz

Kurutma işlemi aromatik bitkiler için önemli bir uygulama olup, bitki materyali ve kurutma yöntemine göre farklılıklar göstermektedir. Bu çalışmada limoni kekik olarak bilinen *Thymus sipyleus* Boiss.var.*sipyleus* yaprakları 4 farklı kurutma yöntemi (Açık havada, mikrodalga, donduruculu kurutucu, 50-70 ºC'de fırında) ile kurutulmuştur. Uçucu bileşenler eşzamanlı destilasyon-ekstraksiyon (SDE) yöntemiyle ekstrakte edilmiştir. Citronellol, 1,8-cineol, camphor camphene ve myrcene bütün örneklerde en önemli bileşikler olarak bulunmuştur. Taze yaprakta % 17,9 olan citronellol miktarı kurutma işlemi ile % 22,7'ye yükselmiştir. Thymol oranı ise farklı kurutma yöntemlerinde % 0,35-3,80 arasında değişmektedir. Kurutma işlemi monoterpen hidrokarbon oranını düşürmüştür (%3-5). Fakat, bu grubun alkol formu ise artmıştır (%1-6). Açık havada kurutma veya 50ºC'de fırında kurutma bu tür için en uygun yöntemdir.

Anahtar Kelimeler: Donduruculu kurutucu, Mikrodalga, Fırında kurutma, Açık havada kurutma, Kekik.

Effect of Drying Methods on the Composition of Volatile Compounds of Thyme (*Thymus sipyleus* Boiss. var. sipyleus)

Abstract

Drying is an important application for aromatic plants and showed variations regard to plant material and drying methods. In this study, aerial parts of *Thymus sipyleus* Boiss.var.*sipyleus* were dried with four different drying methods (Air-dried, Microwave, Freeze-drying, oven drying at 50-70 ºC.) and extracted with Simultaneous Distillation-Extraction (SDE) to determine the volatile compounds. Citronellol, 1,8-cineol, camphor camphene and myrcene were found to be the dominant compounds in all samples. The amount of citronellol increased with drying to 22,7% where this amount was 17,9% in the fresh samples. Thymol was ranging between 0,35-3,80% with different drying methods. Drying procedure decreases (3-5%) the amount of monoterpene hydrocarbons. However, alcohol forms of these compounds were increased (1-6%). Air-drying and 50 ºC oven-drying can be suitable methods for drying of this species.

Keywords: Freeze drying, Microwave drying, Oven-dry, Air-drying, Thyme.

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1. Introduction

Thymus, a genus of *Lamiacea* family, has 38 species and 64 taxa where 24 are, endemic in Turkish flora (Davis, 1982). It is mostly used as flavoring agent (condiment and spice), aromatic - medicinal plant and as herbal tea because of its pleasant aroma. It treats pulmonary, bronchial, digestive, urinary infections and heals some minor wounds. Due to its antioxidant capacity it is used in dietary supplements. Also, it is concluded as a new natural agent for treatment of Acanthamoeba infection. Aerial parts of *T. sipyleus* treat stomachache, gastric ulcer, tonsillitis, urinary system diseases, eczema and hemorrhoids (Tümen et al., 1995; Polat et al., 2007; Topal et al., 2008; Ozgen et al., 2011; Nouasri et al., 2015; Yasar et al., 2016).

Drying, reduction of water content in bio-origin products, aim to reduce packing requirements and shipping weight, to distribute to new markets and prolong the self-life by inhibiting the microorganisms growth and enzymatic reactions. It is also an important factor for pharmaceutical industries, that has to dry plants before extracting the active compounds (Mujundar, A. S. and C. L. Law., 2010; Rahimmalek, M. and S. A. H. Goli., 2013; Saeidi et al., 2016). However, drying may cause severe changes in chemical and physical properties of plants. Drying method, application time and temperature are important parameters affecting the chemical compounds specially volatiles (Calĭn-Sánchez et al., 2015). Common conventional drying methods are hot-air drying (AD), freeze drying (FD) and vacuum drying (VD). Although AD is most popular method, high temperature and long drying times cause non-uniform product quality and degradation of flavor compounds (Szumny et al., 2010). FD gives high quality products. Nevertheless, drying time is long and capital costs, energy consumption is high. Microwave drying (MD) is a modern method and generally combined with AD and vacuum to improve the effectiveness. It has a high heat transfer rate with great energy efficiency. However it is not so common (An et al, 2016, Calĭn-Sánchez et al., 2012).

Composition of volatile compounds of Thymus is widely studied because of its wide usage (Baser et al., 1992a, Baser et al., 1992b, Baser et al., 1992c, Baser et al., 1993a, Baser et al., 1993b, Baser & Koyuncu, 1994, Tümen et al. 1994). To the best of our knowledge, there is no information about the effect of drying method on the chemical composition. Therefore, the objective of this study was to evaluate the effect of drying methods on the composition of volatile compounds of *Thymus sipyleus* Boiss.var.*sipyleus.*

2. Material and Method

2.1. Plant Material

Aerial parts of *Thymus sipyleus* Boiss.var.*sipyleus* was used as a plant material. Samples were collected from Burdur-Büğdüz at 1200 – 1400 altitude. Plant was identified by Mehtap Öztekin (Voucher specimen; MÖ 4053, Centralanatolia Research Center, Ankara). Samples were stored in a freezer till analysis.

2.2. Drying Methods

Four different drying methods were used. Fresh plant material was divided into four groups before drying procedure. Oven drying was performed at 50^0C and 70 ^{0}C for 4h. Freeze-drying was at temperature -50^0C and 0,284 m Bar for 7 h (Telstar Cryodos), Microwave drying at 360 W for 5 min. and air-drying under direct sunlight at 25 ^{0}C for 5 days. Drying conditions were set to achieve 9 % moisture content where American Spice Trade Association demands. TAPPI T-208 om-94 was used to determine the moisture content. Fresh samples were used as control.

2.4. Extraction Procedure

Simultaneous Distillation-Extraction (SDE) was performed with 25 g chopped plant material in 350 mL distilled water and 150 mL diethyl ether for 2 h. Diethyl ether part concentrated in a Vigruex column (40 ^{0}C). Extracts were stored at 4^0C till analysis.
Quantification of volatile compounds was performed with Shimadzu GC-2010 Plus model FID-GC, coupled with TRB-5 (30 m x 0,25 mm id. and 0,25 film thickness) capillary column. Temperature program was 40^0C raised at 4 ^{0}C/min. to 260 ^{0}C (10 min.).Hydrogen was used as a carrier gas with 1:10 split ratio. For qualification, Shimadzu GCMS-QP 2010 model GC-MS was used. Helium was used as a carrier gas with 1,6 mL/min flow rate. Ionization energy was 70 e.V. and mass range 40-700 m/z. Temperature program was as mentioned above. For identification, mass spectra of those from NIST, WILEY and FFNC mass data bank were used.

3. Results and Discussion

With SDE extraction 45 compounds were found in the aerial parts of Thymus (Table 1). Citronellol (17.9%), 1,8-cineol (9.26%) and camphor (6.16%) were found to be the major compounds in the fresh leaves. Baser et al. (1995) reported that geranial (36.9%) and neral (25.6%) were the dominant compounds for the essential oil of *Thymus sipyleus* Boiss.var.*sipyleus.* where the Geranial/neral gave citral. In another study 1.8-cineol was found to be the major compound (19.9-73.8%) in the essential oil of the same thymus species (Yilmaz et al.2004). The amount of thymol in this study was only 0.71%.

Table 1. Composition of volatile compounds of SDE extracts of Thymus with different drying methods

RI	Compounds	Control	AD	MW	FD	Oven-dry 50 °C	Oven-dry 70°C
922	α-thujene	0.31	0.53	0.21	0.23	0.27	0.25
928	**α-pinen**	**4.86**	**5.56**	**4.63**	**3.99**	**3.88**	**3.42**
942	**camphene**	**5.78**	**5.31**	**4.58**	**4.84**	**5.28**	**5.03**
968	sabinen	0.87	0.88	0.69	0.78	0.87	0.87
971	β-pinene	1.48	1.42	1.27	1.26	1.46	1.48
972	octan-3-ol	0.79	0.78	0.57	0.75	0.76	0.56
989	**myrcene**	**5.83**	**5.42**	**4.11**	**4.94**	**5.28**	**5.34**
1013	α-terpinene	0.43	0.79	0.35	0.49	0.49	0.48
1021	p-cymene	1.22	0.95	0.57	0.79	0.90	0.46
1024	limonen	1.70	1.72	1.46	1.87	1.91	1.55
1027	**1-8-cineol**	**9.26**	**8.07**	**7.22**	**7.66**	**9.17**	**9.27**
1034	Z-β-ocimen	0.11	0.14	0.08	0.11	0.11	0.10
1044	E-β-ocimen	0.94	0.81	0.66	0.93	0.86	0.82
1053	δ-terpinene	1.48	1.46	0.86	1.31	1.43	1.07
1061	cis-sabinenhydrate	3.74	3.64	2.74	3.46	3.88	5.94
1084	terpinolen	0.23	0.33	0.21	0.24	0.21	0.24
1094	trans-sabinenhydrate	0.64	0.58	0.44	0.53	0.60	0.61
1098	linalool	2.04	3.40	2.88	3.79	2.63	1.45
1101	pelargonaldyde	0.22	0.24	0.25	0.20	0.20	0.10
1121	rose-oxide	0.73	0.25	0.98	0.64	0.61	0.39
1136	menth-2-en-1-ol	0.17	0.21	0.13	0.17	0.17	0.17
1137	**camphor**	**6.16**	**7.05**	**5.47**	**5.73**	**5.92**	**5.73**
1159	**isoborneol**	**4.87**	**3.99**	**4.61**	**3.72**	**5.19**	**4.73**
1171	terpinen-4-ol	2.01	2.00	1.47	2.01	2.03	1.95
1186	α-terpineol	1.15	0.93	0.88	0.75	0.97	0.90
1222	**citronellol**	**17.9**	**15.9**	**22.1**	**21.8**	**21.3**	**22.7**
1239	neral	2.02	1.80	1.59	1.76	2.05	1.41
1264	geranial	1.75	1.62	1.14	1.31	1.87	1.10
1281	bornylacetat	0.93	0.91	1.04	0.79	0.89	0.96
1289	thymol	0.71	3.80	0.49	0.51	0.49	0.35
1387	β-bourbonene	0.60	0.37	0.40	0.46	0.31	0.21
1389	trans-β-elemen	0.12	0.16	0.00	0.14	0.09	0.08
1442	α-humulene	0.56	0.59	0.46	0.52	0.43	0.35
1458	alloaromadendrene	0.32	0.44	0.38	0.41	0.21	0.21
1475	cadina-1-(6).4-dien	0.23	0.21	0.24	0.28	0.19	0.18
1484	germacren D	1.32	1.47	1.31	1.59	1.00	0.93
1498	bicylogermacrene	1.65	2.27	2.06	2.17	1.60	1.69
1520	δ-cadinene	1.94	1.39	1.82	2.01	1.38	1.16
1552	Delta-Cadinen	-	0.26	0.35	0.30	0.27	0.31
1548	α-elemol	1.70	5.00	3.52	2.68	2.49	5.25
1559	nerolidol	1.99	0.00	3.90	3.76	1.48	1.52
1575	spathylenol	1.66	1.68	2.26	1.33	1.59	1.56
1580	caryophylene oxide	1.45	0.98	1.52	0.98	1.23	0.89
1640	**α-muurolol**	**5.44**	**4.66**	**7.05**	**5.31**	**5.48**	**5.43**
1647	β-eudesmol	0.70	1.13	1.02	0.67	0.58	0.76

RI; Retention Index AD: Air-dry; MW: Microwave-dry; FR:Freeze-Dry.

Different drying methods showed dissimilar results. In the air-dried samples. the amount of thymol and camphor were increased to 3.80% and 7.05% respectively. Venskutonis et al.(1996) reported that the amount of thymol increased after air-drying in *Thymus vulgaris* L.. Some sesquiterpens like germancrene D. bicyclogermacrene and α-elemol were increased. However. the other major compounds citronellol (15.9%) and 1.8-cineol (8.07%) were decreased. Air-drying is the most common and low cost method with some disadvantages such as variable weathering conditions which effect the drying time (Kara et al.2014).

In the oven-dried samples two different temperatures was applied. With the temperature (50-70^{0}C). mono-sesquiterpen hydrocarbons were decreased. However. alcohol forms of these groups such as citronellol (21.3-22.7%). 1.8-cineol (9.17-9.27%) and cis-sabinenhydrate (3.88-5.94%) were increased. Drying temperature is an important parameter affecting the quality and the quantity of the volatiles. Not only the yield of essential oil decreased with temperature but also the color of plant material changed because of the decomposition in the plant cells (Saeidi. K et al. 2016; Rahimmalek and Goli. 2013).

The amount of dominant compound citronellol (22.2%) was increased while thymol (0.49%) and camphor (5.47%) were decreased in microwave drying. Generally. sesquiterpen alcohols showed the highest amounts (%17.7%) in microwave drying. MW has some advantages compared to traditional methods (air-oven dry) such as short drying time and stationary plant color (Kamel et al.2013; Mashkani et al. 2018). For drying of *Thymus vulgaris* L. Calín-Sánchez (2013) recommended vacuum-microwave drying at 240 was a suitable method. In the freeze-dried samples. the amount of citronellol and 1.8-cineol were 21.8% and 7.66% respectively. Thymol (0.51%) and camphor (5.73%) amounts were decreased compared to fresh samples. Freezing temperature is also essential on the loss of volatiles. At high temperatures (-198^{0}C) this decrement is higher (Diaz-Maroto et al.2003)

Drying methods affected significantly the component groups depending on the plant species (Sefidkon et al.2006; Asekun et al. 2007). In this study. Monoterpene (5.7%) and sesquiterpene (6%) alcohols increased after drying procedure (Fig.1) especially in oven-dried and MW samples. However. monoterpene hydrocarbons (6%) and monoterpene aldehydes (1.2%) were decreased after samples were dried. Similar results were reported for different spices (An et al.2016; Venskutonis P.R.1997

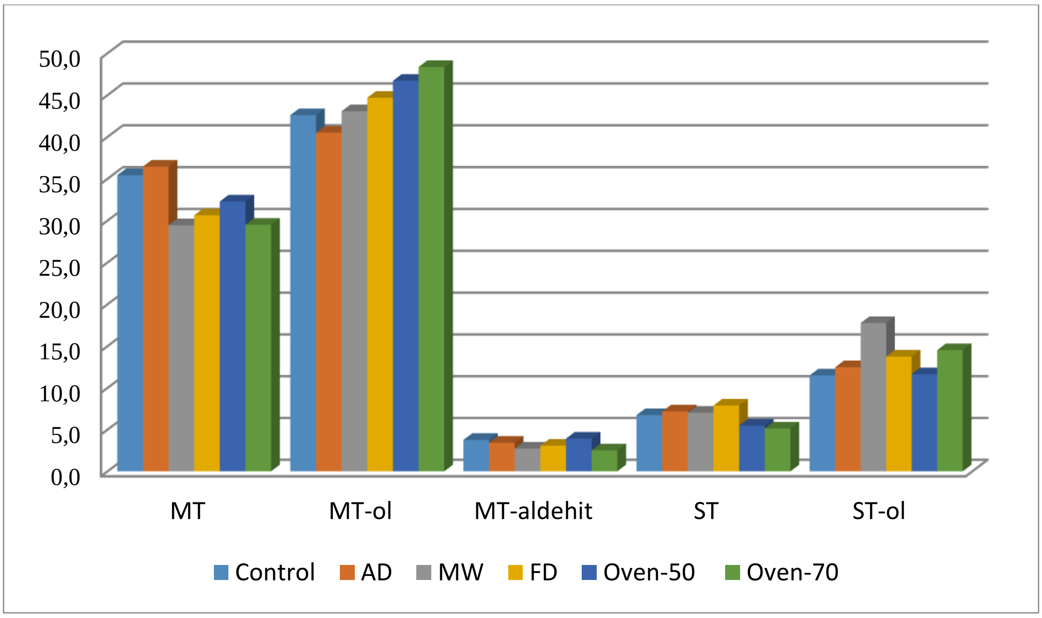

Figure 1. Effect of drying methods on the compound groups of Thymus (%).

4. Conclusion

In this study, citronellol was found to be the major compound in all samples. In the control samples it was 17.9% and in the oven-dry (70 ºC) it was 22.7%. The second important compound was 1,8-cineol with 7.22-9.27% amounts. Freeze-drying and microwave drying decreased the amount of 1,8-cineol. Thymus species classified into two groups as phenol-rich and phenol-poor species for its thymol and carvacrol amount (Tümen et al.1995). According to our results. *Thymus sipyleus* Boiss.var.*sipyleus* belongs to phenol-poor species with 0.71% thymol content. With its fresh form it can be recommended to utilize as herbal tea because of its aromatic odor. For high thymol amount air-drying is more suitable method. However, for high amount of citronellol, 1,8-cineol and to utilize this species as herbal tea oven-drying at 50 ºC is the appropriate method.

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