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Comparison of Tar Produced by Traditional and Laboratory Methods

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ABSTRACT Ethnobotanical uses of plant species varies depending on the knowledge and geography of civilizations, and also prevailing diseases or nuisances in a given time and region. Although parts of annual and/or biennial plants generally have been preferred for ethnobotanical purposes, secondary products such as tar or wood extractives of forest trees have also been used as a natural medicine and coating material. This study compares constituents of tars produced from wood by traditional methods and modern laboratory methods in *Cedrus libani* Achille Richard. In terms of their qualitative and quantitative chemical properties, significant differences were observed between the wood extractives produced by the two methods. Quality of wood used for extraction, extraction temperature and duration also appear to be among the several factors that influence the chemical quality and quantity of extracts. The extent of contribution of each of these factors, either alone or by combination, is not clearly known. In addition, although the products extracted by either method are used for similar purposes, the level of biological effectiveness of each of them and specific chemicals responsible for such effectiveness need to be determined.

INTRODUCTION

Natural products (especially from plants) have been used by people for healing wounds and diseases since ancient times. The use of plant species varies depending on the knowledge and geography of civilizations, and prevailing diseases in a given time and region (Fabricant and Famsworth 2001; Johnson 2006; Ali-Shtayeh et al. 2008). People learned ethnobotanical uses of plants usually by "trial and error" methods in the past. Thus physical, mental, social and practical experiences have been transferred from generation to generation until the present. In other words, evolutionary ancestors of present medicines can be traced back to ethnobotanical experiences accumulated through millennia (Camejo-Rodrigues et al. 2003; Ali-Shtayeh et al. 2008).

Annual and/or biennial plants, rather than woody species, generally have been preferred for ethnobotanical uses (Rivera et al. 2005; Estrada et al. 2007; Kargioglu et al. 2010). However, secondary products of forest trees have also been used widely both as a natural medicine and/or surface coating material in all over the world (Baytop 1999; Zackrisson et al. 2000; Egenberg et al. 2002; Gao et al. 2005; Johnson 2006; Turley et al. 2006; Focho et al. 2009). The Mediterranean Basin, which is considered as one of world's plant biodiversity "hot spots", has more than 100 forest tree species (Fady-Welterlen 2005). The region is also known as one of the "cradles of civilization" on Earth. Woods of some of the trees in the region (*Juniperus* sp., *Pinus* sp., *Betula* sp., *Fagus* sp., *Picea* sp. and *Cedrus* sp.) have been used for tar production since ancient periods. Especially tars of *Pinus sylvestris* Linnaeus (Scots pine) and *Cedrus libani* Achille Richard (Lebanon or Taurus cedar) are considered distinctive due to their historical importance and wide range of application (Baytop 1999; Egenberg et al. 2002; Hjulstrom et al. 2006; Kurt et al. 2008).

Scots pine has a wide distribution range through Europe to Asia (Matyas et al. 2004), one of the most southern natural populations being in Turkey. Its wood has been widely used for building houses, churches, ships and for making various household and farm utensils since ancient times. Also, extract (tar) obtained from its resinous heart-wood has been highly valued export products from the Hanseatic period to the present in Scandinavian countries (Egenberg et al. 2002; Hjulstrom et al. 2006). In comparison with Scots pine, Taurus cedar has relatively small distribution ranges in the eastern Mediterranean Basin. The widest distribution range of the species occurs on the Taurus

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Mountains near Antalya in southern Turkey. It also has small populations and protected stands in Syria and Lebanon (Boydak 2003). Taurus cedar has been highly valued due to its wood material as well as non-wood products such as tar and essential oils since ancient times (Loizzo et al. 2007; Kurt et al. 2008; Cetin et al. 2009).

Tar and essential oils are obtained from Scots pine and Taurus cedar both by traditional methods (Egenberg et al. 2002; Hjulstrom et al. 2006; Kurt et al. 2008) and by using modern laboratory equipment (Hafizoglu 1987; Saab et al. 2005; Ekeberg et al. 2006). These products have been used against various insects, viruses, bacteria, and various human and/or animal diseases (Kizil et al. 2002; Loizzo et al. 2007, 2008; Cetin et al. 2009). Tar is also used as a coating material for wooden surfaces inside and outside of houses, churches, boats and ships (Egenberg et al. 2003; Hjulstrom et al. 2006). Qualitative and quantitative differences between chemical composition of tars produced traditionally and under laboratory conditions have been reported by several authors (Ekeberg et al. 2006; Kurt et al. 2008; Loizzo et al. 2008). Even the tar obtained from the first barrel varies significantly in their chemical composition than the last barrel in the same extraction process (Egenberg et al. 2003).

The aim of this study is to compare chemical compositions of wood extracts (tars) produced by traditional methods with that of modern laboratory methods in Taurus cedar. Specifically, the aims of the study were to 1) describe and compare the two methods, 2) indicate and discuss the differences in chemical composition of tars obtained by the two methods, 3) discuss if there are any differences between biological activities of tars produced by the two methods.

METHODOLOGY

The researchers visited the remote villages and observed traditional tar production at Gecmen village in the Elmali district on the Taurus Mountains in southern Turkey where the most extensive natural stands of Taurus cedar grow. They interviewed the local people and collected information on the traditional uses of cedar tar in the area. The researchers also reviewed the literature about traditional and laboratory methods of tar production on Scots pine for comparative purposes.

Traditional Method

In spite of limited differences in traditional methods for tar production applied on Scots pine (Egenberg et al. 2003; Hjulstrom et al. 2006) and Taurus cedar (Kurt et al. 2008; Kargioglu et al. 2010), general process applied on both species is quite similar. Resinous heartwood material rather than any given portion of a stem is preferred from old stumps of trees. Old stumps (died about 10 to 50 years before) are selected in a hot and dry summer season, mainly due to their very low water contents in summer (Egenberg et al. 2002; Kurt et al. 2008). The resinous heartwoods are then chopped into smaller pieces (10-40 cm length and 2-5 cm thickness). These pieces are stocked and burned in kiln and/or excavated holes on the ground (called *"kurna"* by the native people in southern Turkey) (Kurt et al. 2008). During the burning process, temperatures usually remain above 300 ºC. The extraction process may take up 2-15 days depending on the size of kiln or holes and amount of resinous heartwoods (Egenberg et al. 2002, 2003; Hjulstrom et al. 2006; Kurt et al. 2008). The traditional methods as applied on Taurus cedar and Scots pine were illustrated and discussed in detail by Kurt et al. (2008) and Hjulstrom et al. (2006), respectively.

Laboratory Conditions

Usually, parts of stem from fresh and/or newly cut trees are used to obtain tar under modern laboratory conditions. The stump is chopped into smaller pieces depending on the size of extraction apparatus. The small pieces (2-5 cm) of stump are dried at room temperature and placed into extraction apparatus (Hafizoglu 1987; Loizzo et al. 2008). The extraction temperature is generally arranged between 40 to 100 ºC. Different solvents (such as ethanol and acetone) are used during the extraction process. The laboratory methods are known as hydro distillation due to use of solvents. The extraction period may take up 2-12 hours depending on various factors such as proportion of tar in wood and amount of plant material (Hafizoglu 1987; Kizil et al. 2002; Loizzo et al. 2008).

RESULTS

In traditional methods of extraction (Kurt et al. 2008), Taurus cedar tar contained 83 differ-

ent components, 17 of which made up 86 % of the compound (Table 1). The proportion of sesquiterpenoids in traditional process was 47.6 %, whereas it ranged from 19% to 75% in studies based on laboratory extractions (Hafizoglu 1987; Baser and Demircakmak 1995; Saab et al. 2005; Loizzo et al. 2008). Similarly, although the himachalol component has been reported to be quite high under laboratory studies (32.4 % in Hafizoglu 1987, and 22.5 % in Loizzo et al. 2008), it was not detected at all in traditional method (Kurt et al. 2008). The himachalol as well as atlantones compounds were not also detected both in pine tar and juniper tar (Reunanen et al. 1996). Hydrocarbons with both high- and low-molecular weights were also relatively high (34.7%) in tar produced by traditional method (Kurt et al. 2008). However, they were either not detected and/or were very low in samples obtained under modern laboratory conditions (Hafizoglu 1987; Reunanen et al. 1996; Loizzo et al. 2008). These results suggest that extracts produced by the laboratory methods (Loizzo et al. 2007) may not fully represent the extracts produced by traditional methods (Kurt et al. 2008, Table 1) or vice versa. Indeed, Egenberg et al. (2003) observed that Scots pine tar derived from different stages in kiln production varies significantly in their chemical composition both quantitatively and qualitatively, probably due to dehydrogenation and decarboxylation of the components.

Table 1: Constituents of *tar* of Taurus cedar by different researchers

Compounds	*Kurt et al.(2008) (%)^{T}*	*Loizzo et al.(2008) (%)^{M}*	*Hafizoglu (1987) (%)^{M}*
Monoterpenoids			
m-cymene	1.10	-	-
Monoterpenalcohol	-	-	2.80
Sesquiterpenoids			
β-himachalene	21.17	21.90	3.10
α-himachalene	5.90	10.50	1.50
γ-himachalene	5.46	9.10	-
γ-Dehydro-ar-himachalene	-	0.40	-
ar-himachalene	-	trace	-
z-α-atlantone	7.40	2.10	4.40
E-α-atlantone	-	0.82	-
z- γ-atlantone	-	1.72	-
E-γ-atlantone	-	1.73	-
Himachalol	-	22.50	32.40
Allohimachalol	-	3.20	-
Longibomeol	-	0.80	-
Manool	-	1.70	-
Tumerone	4.50	-	-
Tumerone	1.00	-	-
Chamigran-9-one	2.18	-	-
Sesquiterpenketone	-	-	5.10
Sesquiterpenhydrocarbon	-	-	3.70
Hydrocarbons			
Heptane	15.38	-	-
Cyclohexane	3.92	-	-
Benzene	1.27	-	-
Hexane	1.23	-	-
Heptacosane	5.29	-	-
Eicosane	4.31	-	-
Cyclotrisiloxane	1.13	-	-
Nonacosane	2.18	-	-
Aziridines			
2-aziridinedicarboxylate	2.55	-	-
Ketones			
Ketone	-	-	5.70
New ketone	-	-	5.80
Others	14.09	20.33	35.5
Grand total	100.00	100.00	100.00

Extraction methods: T: traditional, M: modern

DISCUSSION

Chemical composition of tars may change depending on many factors including the types of plant tissues and the process applied (Egenberg et al. 2002, 2003). There may be several reasons as to why the tars produced under these two different methods contain different chemical compounds. Three of them are discussed below.

Wood Material Used (Lightwood versus Heartwood)

In traditional way, the native people prefer dry resinous heart wood from large tree stumps dead for about 10 or more years. Highly resinous dry wood is considered as good quality wood for tar production. Using less resinous and/or moist wood in extraction process lead to lower quality of tar (See Egenberg et al. (2002) and Kurt et al. (2008) for good quality tar in detail). Under modern laboratory conditions wood samples generally are taken from living (or newly cut) trees, dried and then processed for extraction (Hafizoglu 1987; Loizzo et al. 2008). Old, dead resinous stumps produce better quality tar than relatively fresh and newly cut stumps, and extracts produced in autumn (in other words, following a prolonged hot and dry summer) are of higher quality than those produced in other seasons (Kurt et al. 2008).

Extraction Temperature

In the traditional process, temperature inside the system usually reaches above 300 °C. Slow

and regular burning of resinous heartwoods inside the *"kurna"* system improves the quality of tar (Hjulstrom et al. 2006; Kurt et al. 2008). Egenberg et al. (2003) indicated that Scots pine tar obtained from the first barrel in kiln production varies significantly in chemical composition than the last barrel in the same extraction process due to gradual increase of temperature during production. Similar results were reported by Kurt et al. (2008) for traditional tar production from Taurus cedar. Variation in temperature affects dehydrogenation, decarboxylation and aromatization of compounds, thus, causing significant variation in chemical composition of the final product extracted. The good quality tar (in color, viscosity) is obtained from kilns or holes *(kurna)* above 200 ºC (Egenberg et al. 2002, 2003; Kurt et al. 2008).

The low extraction temperature (generally between 40-100 ºC) appears to be not sufficient to induce certain chemical reactions such as dehydrogenation, decarboxylation and others to take place under modern laboratory conditions (Hafizoglu 1987; Loizzo et al. 2008). Also, tar obtained by hydro distillation with solvents (Hafizoglu 1987; Loizzo et al. 2008) appears to have different chemical composition due to oxidation compared to tar obtained by dry and/or destructive distillation (Egenberg et al. 2002, 2003; Kurt et al. 2008).

Heating and/or Burning Time

In traditional methods, the burning duration varies depending on the size of kiln and or *kurna* (excavated holes), the proportion of resins in wood and accuracy of the burning process. It may take up to 2-15 days to complete the whole burning of resinous wood within the kilns and/or *kurna* (Egenberg et al. 2002; Hjulstrom et al. 2006; Kurt et al. 2008). The good quality tar is obtained by burning process that proceeds slowly and gradually during the process (Egenberg et al. 2003; Kurt et al. 2008). In modern laboratory methods, however, the extraction process is completed generally within a few hours (Loizzo et al. 2008). Tar produced under laboratory conditions does not have a desired quality both in color and viscosity according to native people (Kurt et al. 2008).

Biological Activity

The native people consume Taurus cedar tar both internally and externally to heal wounds, fight parasites, and cure various diseases in both human and domestic animals (Baytop 1999; Kurt et al. 2008; Kargioglu et al. 2010). The local people apply Taurus cedar tar (in rather low concentration) in drinking water of domestic animals to protect them against internal parasites and various diseases (Fig. 1). Taurus cedar tar is also used externally against skin wounds and diseases of domestic animals, especially the young and less experienced ones (Fig. 2). Taurus cedar extracts were applied in different areas to investigate their effects on antimicrobial (Digrak et al. 1999; Yesilada et al. 1999; Kizil et al. 2002), antiviral (Loizzo et al. 2008) and larvicidal (Cetin et al. 2009) activities. Also, Singh and Agarwal (1988) reported that α-himachalene and himachalol from *Cedrus deodara* woods had significant insecticidal activity.

Tar of Scots pine has generally been used as a coating material of wooden surfaces of churches, houses, boats and ships (Zackrisson et al. 2000; Egenberg et al. 2002). Scots pine tar is a well known product in Scandinavian countries by the name of "Stockholm tar" (Egenberg et al. 2003; Hjulstrom et al. 2006). Essential oils and tar components from different parts of forest trees (such as needle, cone, root and bark) are known to contain monoterpenes, sesquiterpenes, resin acids, aldehydes, phenols and others (Hafizoglu 1987; Hafizoglu and Reunanen 1987; Baser and Demircakmak 1995; Reunanen et al. 1996; Willfor et al. 2007). Additional studies are needed to investigate if biological activities of tars on various applications differ depending on the kinds of extraction methods.

CONCLUSION

Studies by the researchers indicate that resinous wood extract (or tar) obtained from traditional method has different chemical compounds and/or different amounts of a given chemical compound than that produced under modern laboratory conditions. Such differences in tar composition between the two methods may arise due to several reasons, among which are properties of wood material used, extraction temperature, and length of heating and/or burning time. Tar obtained by either method has been used for similar purposes, regardless of their chemical constituents. However, it is not known

Fig. 1. Application of Taurus cedar tar in drinking water of domestic animals near a high meadows (Photo: Yusuf Kurt)

Fig. 2. Use of Taurus cedar tar for skin diseases on a very young goat (Photo: Yusuf Kurt)

whether tar produced by both methods have similar biological activities or not.

RECOMMENDATIONS

It is suggested that a biological activity study needs to be performed by using tar obtained through both methods, provided both methods use wood material with similar properties.

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REFERENCES

Ali-Shtayeh MS, Jamous RM, Al-Shafie JH, Elgharabah WA, Kherfan FA et al. 2008. Traditional knowledge of wild edible plants used in Palestine (Northern West Bank): A comparative study. *J Ethnobiol Ethnomed*, 4: 13.

Baser KHC, Demircakmak B 1995. The essential oil of Taurus Cedar (*Cedrus libani* A. Rich.): Recent results. *Chem Nat Comp*, 31: 16-20.

Baytop T 1999. *Therapy with Medicinal Plants in Turkey (Past and Present)*. No: 3255 2nd Edition. Istanbul, Trukey: Publications of Istanbul University (in Turkish), P. 480.

Boydak M 2003. Regeneration of Lebanon cedar (*Cedrus libani* A. Rich.) on karstic lands in Turkey. *For Ecol Manage*, 178: 231-243.

Camejo-Rodrigues J, Ascensao L, Bonet MA, Valles J 2003. An ethnobotanical study of medicinal and aromatic plants in the Natural park of "Serra de Sao Mamede" (Portugal). *J Ethnopharmacol*, 89: 199-209.

Cetin H, Kurt Y, Isik K, Yanikoglu A 2009. Larvicidal effect of *Cedrus libani* seed oils on mosquito *Culex pipiens*. *Pharm Biol*, 47 (8): 665-668.

Digrak M, Ilcim A, Alma MH 1999. Antimicrobial activities of several parts of *Pinus brutia, Juniperus oxycedrus, Abies cilicia, Cedrus libani* and *Pinus nigra*. *Phytother Res*, 13: 584-587.

Egenberg MI, Aasen JAB, Holtekjolen AK, Lundanes E 2002. Characterisation of traditionally kiln produced pine tar by gas chromatography-mass spectrometry. *J Anal Appl Pyrol*, 62: 143-155.

Egenberg MI, Holtekjolen AK, Lundanes E 2003. Characterisation of naturally and artificially weathered pine tar coatings by visual assessment and gas chromatography-mass spectrometry. *J Cult Herit*, 4: 221-241.

Ekeberg D, Flaete PO, Eikenes M, Fongen M, Naess-Andresen CF 2006. Qualitative and quantitative determination of extractives in heartwood of Scots pine (*Pinus sylvestris* L.) by gas chromatography. *J Chromatogr A*, 1109: 267-272.

Estrada F, Villareal JA, Cantu C, Cabral I, Scott L, Yen C 2007. Ethnobotany in the Cumbres de Monterrey National Park, Nuevo Leon, Mexico. *J Ethnobiol Ethnomed*, 3: 1-8.

Fabricant DS, Famsworth NR 2001. The value of plants used in traditional medicine for drug discovery. *Environ Health Perps*, 109 (1): 69-75.

Fady-Welterlen B 2005. Is there really more biodiversity in Mediterranean forest ecosystems? *Taxon*, 54 (4): 905-910.

Focho DA, Newu MC, Anjah MG, Nwana FA, Ambo FB 2009. Ethnobotanical survey of trees in Fundog, Northwest Region, Cameroon. *J Ethnobiol Ethnomed*, 5:17.

Gao Y, Jin YJ, Li HD, Chen HJ 2005. Volatile organic compounds and their roles in bacteriostasis in five conifer species. *Acta Botanica Sinica*, 47 (4): 499-507.

Hafizoglu H 1987. Studies on the chemistry of *Cedrus libani* A. Rich. I. Wood extractives of *Cedrus libani*. *Holzforschung*, 41 (1): 27-38.

Hafizoglu H, Reunanen M 1987. Studies on the chemistry of *Cedrus libani* A. Rich. IV. Suberin composition of the cedar bark. *Holzforschung*, 41 (4): 261-263.

Hjulstrom B, Isaksson S, Hennius A 2006. Organic geochemical evidence for pine tar production in middle Eastern Sweden during the Roman Iron Age. *J Archaeol Sci*, 33: 283-294.

Johnson ML 2006. Gitkson medicinal plants-cultural choice and efficacy. *J Ethnobiol Ethnomed*, 2: 29.

Kargioglu M, Cenkci S, Serteser A, Konuk M, Vural G 2010. Traditional uses of wild plants in the Middle Aegean region of Turkey. *Hum Ecol*, 38: 429-450.

Kizil M, Kizil G, Yavuz M, Aytekin C 2002. Antimicrobial activity of resins obtained from the roots and stems of *Cedrus libani* and *Abies cilicia*. *Appl Biochem Micro+*, 38 (2): 144-146.

Kurt Y, Kacar MS, Isik K 2008. Traditional tar production from *Cedrus libani* A. Rich. on the Taurus Mountains in southern Turkey. *Econ Bot*, 62 (4): 615-620.

Loizzo MR, Saab AM, Statti GA, Menichini F 2007. Composition and á-amylase inhibitory effect of essential oils from *Cedrus libani*. *Fitoterapia*, 87 (4): 323-326.

Loizzo MR, Saab AM, Tundis R, Statti GA, Lampronti I et al. 2008. Phytochemical analysis and *in vitro* evaluation of the biological activity against herpes simplex virus type 1 (HSV-1) of *Cedrus libani* A. Rich. *Phytomedicine*, 151 (2): 79-83.

Matyas C, Ackzell L, Samuel CJA 2004. *EUFORGEN Technical Guidelines for Genetic Conservation and Use for Scots Pine (Pinus sylvestris)*. International Plant Genetic Resources Institute, Rome, Italy.

Reunanen M, Ekman R, Hafizoglu H 1996. Composition of tars from softwoods and birch. *Holzforschung*, 50 (2): 118-120.

Rivera D, Obon C, Inocencio C, Heinrich M, Verde A et al. 2005. The ethnobotanical study of local Mediterranean food plants as medicinal resources in southern Spain. *J Physiol Pharmacol*, 56: 97-114.

Saab AM, Harb FY, Koenig WA 2005. Essential oil components in heart-wood of *Cedrus libani* and *Cedrus atlantica* from Lebanon. *Minerva Biotechnol*, 17 (3): 159-161.

Singh D, Agarwal S 1988. Himachalol and beta-himachalene: Insecticidal principles of Himalayan cedarwood oil. *J Chem Ecol*, 14 (4): 1145-1151.

Turley DB, Chaudhry Q, Watkins RW, Clark JH, Deswarte FEI 2006. Chemical products from temperate forest tree species-Developing strategies for exploitation. *Ind Crop Prod,* 24: 238-243.

Willfor S, Hafizoglu H, Tumen I, Yazici H, Arfan M et al. 2007. Extractives of Turkish and Pakistani tree species. *Holz Roh Werkst,* 65: 215-221.

Yesilada E, Gurbuz I, Shibata H 1999. Screning of Turkish anti-ulcerogenic folk remedies for anti-*Heliobacter pylori* activity. *J Ethnopharmacol,* 66: 289-293.

Zackrisson O, Ostlund L, Korhanen O, Bergman I 2000. The ancient use of *Pinus sylvestris* L. (Scots pine) inner bark by Sami people in northern Sweden, related to cultural and ecological factors. *Veg Hist Archaeobot,* 9: 99-109.