Original Article

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Chemical comparison of eleven cinnamon aromatic water samples from Fars (Iran) local markets with a standard sample

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Abstract

Current study aimed to chemically assess the volatile constituents of eleven commercial cinnamon hydrosols purchased from Fars province (Iran) local markets in comparison to a standard sample. Via a liquid extractor, the volatile oil fractions of the samples and the standard hydrosol, yielded from essential oil extraction of an authenticated cinnamon bark sample, were recovered. Gas chromatography/ flame ionization detector (GC/FID) and subsequently GC/MS (GC/mass spectroscopy) were employed to assess and identify the chemical compositions of the prepared samples. The analysis resulted in a total of 25 components. Cinnamaldehyde was found as the main constituent in ten populations (S2-S11), as well as in the standard sample (63.04-91.61%). Considerable amounts of dibutyl phthalate, as a common plasticizer, were also detected in all samples. This is the first report of analysis and identification of volatile constituents in cinnamon hydrosol, a common medicinal beverage. Although high amount of cinnamaldehyde in cinnamon hydrosol can introduce this tasty medicinal beverage for further studies similar to the respective botanical part or various usual extracts, more comprehensive monitoring is to be performed on safety, purity, and quality of such preparations.

Keywords: Aromatic water, Cinnamomum verum J.Presl, GC/MS, Hydrosol, Volatile constituent.

1. Introduction

Cinnamon or Cinnamomum verum J.Presl (Lauraceae) is a small evergreen tree, 10-15 m tall, and native to subcontinent of India and nearby countries (1). From this medicinal plant, the bark is mainly a spice and flavoring agent with important medicinal properties (2). In addition to the culinaric uses, biologically active substances in cinnamon barks are responsible for various related pharmacological activities.

Current reports have revealed the antimicrobial (3), antifungal (4), antioxidant (5), nematicidal (6), analgesic (7), antidiabetic (8, 9), α-amylase inhibitory (10), anti-cholinesterase (11), neuroprotective (12), anticancer (13), anti-acne (14), hypotensive (15), and lipid lowering (16) activities of cinnamon botanical parts. These numerous properties are due to the presence of a variety of chemical compositions and different classes of metabolites in this medicinal plant (17).

Cinnamon essential oil is known as a popular product of fresh and aged barks with numerous medical and pharmacological properties. It is reported that the spicy taste of cinnamon is due to the presence of cinnamaldehyde, a major resinous

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compound observed in the essential oil (18).

In addition to the cinnamon essential oil, the yielded hydrosol, floral or aromatic water is also spoken of as a medicinal preparation with similar but weaker effects compared to the original oil. Cinnamon hydrosol which is extensively marketed as a medicinal drink in Iran and nearby countries, is a byproduct obtained during the extraction of cinnamon essential oil. Hydrosols usually contain some water soluble parts of the yielded essential oil (19). Medical and pharmacological properties of hydrosols, subsequent to the essential oils, introduce these products as the next aromatherapy. In addition to essential oils, hydrosols may be used in aromatherapy considering their medical and pharmacological properties (20).

Although there are numerous reports on the composition analysis of cinnamon essential oil, no comprehensive studies have been performed on the chemical constituents of cinnamon hydrosol. Accordingly, the current study is intended to chemically assess the volatile constituents of different commercial cinnamon hydrosols compared to a standard sample.

2. Methods

2.1. Sample preparation

Eleven various samples of cinnamon hydrosols were prepared from traditional medical markets of Fars province (south of Iran). These hydrosols were numbered from 1 to 11. To draw a comparison among those samples, a batch of cinnamon bark was purchased, botanically authenticated, and subjected to hydrodistillation to yield a standard hydrosol. The resultant samples were kept in the fridge (4 ºC) for further steps.

2.2. Essential oil recovering and concentration

Via a liquid extractor, the volatile oil fractions of purchased samples and the obtained standard hydrosol were recovered in two subsequent steps. At the beginning, 500 ml of each sample was added to petroleum ether (500 ml) as a solvent. The solvent was then heated to 45ºC for around 150 min to recover the essential oil from the aqueous phase into the organic fraction. The new organic phase from the first stage was extracted and subsequently, fresh petroleum ether (500 ml) was added to the system to increase the essential oil yield in the organic phase (21). The mixture was again heated for 150 min. The recovered essential oil of each sample was then individually concentrated via basic rotary evaporator connected to a vacuum pump. All recovered samples were kept in amber glass vials for further investigation.

2.3. Gas chromatography and components analysis

Gas chromatography/ flame ionization detector (GC/FID) analysis was carried out on a gas chromatograph Agilent Technologies (7890A) apparatus equipped with a HP-5 column (25 m length×0.32 mm i.d.; film thickness 0.52 µm) connected to a FID. Nitrogen was used as the carrier gas (flow rate: 1 ml/min, split ratio: 1:30) and injector and detector temperatures were adjusted at 250 and 280 °C, respectively. Column temperature was linearly programmed from 60 to 250 °C (at a rate of 5°/min) and subsequently was held at 250 °C for approximately 10 min.

The adjusted GC/FID method and condition were employed for GC/MS (GC/mass spectroscopy) analysis. The process was performed via an Agilent Technologies (7890 A) gas chromatograph with a HP-5MS capillary column (phenyl methyl siloxane coated, 30 m×0.25 mm i.d.) connected to a mass detector (Agilent Technologies model 5975 C). The flow rate of the carrier gas, Helium, was adjusted at 1 ml/min. The mass spectrometer was acquired in EI mode (70 eV; mass range: 30-600 m/z). The interface temperature was set at 280 °C.

A homologous series of n-alkanes C8-C30 was injected to GC/MS in order to facilitate the process of determination of the component verification via calculating the Kovats indices (KI). Identification of components was based on a comparison of their mass spectra with Willey (nl7), libraries of spectra (Adams') and with those reported in the related literatures.

3. Results and Discussion

In this study, the identification of 91.93-99.30% of total volatile constituents of employed hydrosols was carried out. The analysis procedure revealed a total number of 25 components. Table 1 represents the chemical compositions of all samples. Cinnamaldehyde was found as the main

constituent in ten samples (S2-S11) in addition to the standard sample (93.37% in the standard and 63.04-91.61% in test samples). According to the standard sample, only one main ingredient should be present in the essential oil of the cinnamon hydrosol (Cinnamaldehyde >90%). However, a variety of constituents was seen in one of the test samples (S1). The chemical compositions in this sample was also much more than in other samples. thymol (14.16%), carvacrol (14.21%), trans-cinnamic acid (12.47%), cinnamaldehyde (12.20%), and carvone (6.25%) were found as the main components of S1. As there is no report on the presence of thymol or carvacrol in cinnamon essential oil (22), presence of these compounds in the respective hydrosol represents impurities. Therefore, S1 can be introduced as the most inferior sample among the studied populations (Table 1).

Apart from the compounds related to the hydrosol samples, considerable amounts of dibutyl

Table 1. Volatile constituents of different cinnamon hydrosols.

Component	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	STD	KI-C	KI-R	Ref.
Benzaldehyde	-	-	1.60	-	0.65	-	1.42	2.32	-	-	-	-	960	961	(35)
1,8-Cineole	0.76	-	-	-	-	-	**9.35**	-	2.07	1.16	2.32	-	1033	1033	(36)
Acetophenone	0.26	-	-	-	-	-	-	-	-	-	-	-	1078	1076	(37)
Linalool	-	0.86	-	-	-	-	1.60	-	-	-	-	-	1100	1103	(38)
Benzenepropanal	0.20	-	-	-	1.52	-	-	-	-	-	1.81	-	1162	1160	(39)
1-Borneol	0.62	-	-	-	-	-	-	-	-	-	1.13	-	1168	1173	(40)
Alpha-Terpineol	1.31	1.09	-	-	-	-	3.36	-	1.78	3.15	3.20	-	1192	1195	(41)
Berbenone	-	-	-	0.92	-	-	-	-	-	-	-	-	1212	1214	(42)
Benzenepropanol	1.93	-	-	-	-	-	-	-	-	-	-	-	1233	1233	(43)
Pulegone	0.98	-	-	-	-	-	-	-	-	-	-	-	1242	1244	(44)
Dihydrocarvone	2.94	-	-	2.29	-	-	-	-	-	-	-	-	1246	1242	(45)
Carvone	**6.25**	-	-	-	-	-	-	-	-	1.25	-	-	1247	1246	(46)
Cinnamaldehyde	**12.20**	**84.28**	**91.61**	**83.46**	**63.04**	**89.88**	**73.01**	**87.28**	**85.00**	**72.62**	**71.12**	**93.37**	1276	1277	(47)
Borneol acetate	-	-	-	-	-	-	-	-	-	-	0.75	-	1286	1286	(48)
Thymol	**14.16**	-	-	-	-	-	-	-	-	-	1.01	-	1292	1290	(49)
Carvacrol	**14.21**	-	-	-	-	-	-	-	-	-	-	-	1302	1303	(50)
Cinnamyl alcohol	2.30	-	-	-	3.61	-	-	-	-	1.53	1.04	-	1309	1314	(51)
Hydrocinnamic acid	0.16	-	-	-	-	-	-	-	-	-	-	-	1339	1343	(52)
Piperitenone	0.41	4.81	-	-	-	-	-	-	-	-	-	-	1344	1344	(53)
Cumarin	0.33	-	-	-	**6.45**	-	-	-	2.57	1.01	6.56	-	1439	1439	(54)
E-cinnamyl acetate	3.60	-	-	2.41	4.53	-	-	1.24	-	4.69	4.01	-	1441	1443	(55)
trans-Cinnamic acid	**12.47**	1.34	1.11	1.52	4.61	1.67	0.92	1.81	-	3.16	-	-	1458	1457	(56)
Methyl hexadecanoate	1.84	-	-	-	1.15	-	-	-	-	-	-	-	1926	1926	(57)
Dibutyl phthalate	**14.54**	1.94	2.45	**5.63**	**10.49**	3.39	2.50	2.59	4.86	3.61	**6.35**	4.08	1965	1967	(58)
Methyl stearate	0.46	-	-	-	-	-	-	-	-	-	-	-	2126	2127	(59)
Identification	**91.93**	**94.32**	**96.77**	**96.23**	**96.05**	**94.94**	**92.16**	**95.24**	**96.28**	**92.18**	**99.30**	**97.45**			

phthalate, as a common plasticizer, which is freely soluble in organic solvents such as petroleum ether and n-Hexane, was also detected in all samples. The level of this composition in samples varied from 14.54% in S1 (the most inferior sample) to 1.94%. Samples 4, 5, and 11 also contained large amounts of dibutyl phthalate. Actually, this ingredient is a fraction or derivative of plasticizers or polyethylene terephthalate (PET) containers. Keeping the hydrosol in big PET containers is one of the main reasons for the appearance of dibutyl phthalate. High amounts of this compound in oral samples may be harmful for the kidneys, liver, and central nervous system (23).

Similar to that of the hydrosol, cinnamaldehyde is the main constituent of cinnamon bark (24). As a derivative of acrolein, cinnamaldehyde is a benzene ring attached to an unsaturated aldehyde (25). Because of the high amount of cinnamaldehyde in cinnamon hydrosol, several useful therapeutic effects can be anticipated for the containing hydrosol. Cinnamaldehyde has shown various pharmacological and pharmaceutical activities in the previous studies. As a fragrance ingredient, this constituent is widely used in numerous cosmetic preparations. Studies have shown potent antibacterial, antifungal, and anthelmintic activities of this medicament (24, 26, 27). An investigation demonstrated that this compound is able to protect the brain of mouse models against cerebral ischemia injury, based on its effects on oxidative reactions and inflammation (28). This medicament has also repeatedly exerted antioxidant and radical scavenging activities in experimental and animal studies (29, 30). Cinnamaldehyde also possess analgesic and anti-inflammatory effects (29). Other pharmacological activities, such as preventive effect against organ toxicity, contribution in provoking the insulin sensitivity, and protecting the endothelial dysfunction under high concentration of glucose are also attributed to this constituent (31-33).

Extracted hydrosols of different medicinal plants are used for medicinal and pharmaceutical approaches (34). Cinnamon hydrosol is one of those preparations used as a medicinal drink in folk Iranian medicine. Considering the various properties reported for cinnamaldehyde, the respective hydrosol could also be used for pharmacological and chemical studies.

4. Conclusion

Results of this study demonstrated that similar to the cinnamon essential oil, the yielded aromatic water, which contains more than 90% of cinnamaldehyde, could be mentioned as a medicinal fraction of cinnamon. Therefore, this type of beverage can be introduced as a source of cinnamaldehyde, for related medicinal approaches. Current work also reported the presence of phthalate in many aromatic water samples, mainly related to the maintenance procedure and containers. Based on the chemical assessment of different cinnamon hydrosols, it is of most concern that more monitoring processes should be considered to ensure the quality and safety of those preparations.

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Conflict of Interest

None declared.

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