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An IR spectroscopic investigation of tarhana

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KEYWORDS: *tarhana, IR spectroscopy, discrimination, traceability, quality, commercial, home-made*

ABSTRACT: *Tarhana is a popular Turkish fermented wheat-yogurt mixture for soup making. This traditional food is widely consumed in Turkey. In the last decades, tarhana has been produced commercially in factory. Ingredients of tarhana both homemade and fabricated are display variations. Quality control of tarhana is becoming a problem. The IR spectra of 12 commercial (COM) or home-made (HM) samples were investigated. The T% values were constantly inferior in the HM (-15%) sign of a richer content. Along the spectra from 4000 to 400 cm-1 the F fisher's test of single wavelength differentiated maximally the two types at 402 cm-1(P=0.23), but a wavelength selection process clusterized 6 bands (2476, 1596, 1364, 608, 596, 402 cm-1). A multiple regression was developed on the six bands in a discriminative equation provided by a R2 0.92 (R2adj 0.83). After full cross-validation the R2 values descended to 0.65, but only 1 sample of COM type was missed as HM. Some hypothesis concerned the implicated bands in regards to a different vitamin B3 (Niacine) contents. IR spectroscopy is a useful tool to identify a sample due to its unique results. FTIR Spectra results show that vibrational frequencies can be specific data to confirm the quality and traceability of tarhana.*

INTRODUCTION

One of the oldest traditional Turkish soups, tarhana has been locally consumed for many generations. Products similar to “Tarhana” in Turkey are known as the Cypriot “Trachanas”, “Kishk” in Egypt, Syria and Jordan, “Kushuk” in Iraq and “Tahonya/Talkuna” in Hungary and Finland (1). The protein and vitamin contents of tarhana make it one of the most important foods (2-4). Also, in the folk culture, it is believed that tarhana cures some basic illnesses (like sore-throats, stomach-aches, colds and flues) Methods for preparation and amount of ingredients may vary from one place in Turkey (5, 6). A great deal of attention has been paid towards healthy foods; therefore there is a growing commercial interest in producing tarhana. In addition to that, tarhana has got a 2-3 years shelf life (7). This fact encourages producers in food industry. Promoting tarhana industrial production is risky, because consumers demand nutritious and healthier food. Rapid quality control of tarhana has become a serious problem. The microbiological, physical and chemical hazards have been examined by scientists (7-10)

IR spectroscopy is a useful tool for rapid investigation of the structural properties in foods (11-13). And also IR spectroscopy can provide much more information on the characteristics, composition and chemical structure of a sample. Control in food industry is very complex process. There are lots of methods for defining the contaminants, additives, pathogens, microbial activities, by quality control in the food industry. But using IR device in the food industry is the most cost-effective solution. Less toxic chemicals are needed to investigate tarhana in IR spectroscopy.

In this study, the properties of tarhana were investigated for the first time in the literature by monitoring identical vibrational frequencies using IR spectroscopy.

MATERIAL AND METHODS

Commercial tarhana (half of 12) samples which were purchased from shops and the other of the samples are home-made. All samples are used in their rigid form. The spectra of samples were recorded at room temperature using a Perkin Elmer BX II FTIR device set to standard parameters (4000-400 cm-1, 1801 points). Samples were prepared in the form of potassium bromide pellets containing 1/100 ratio of sample/ KBr and they were mixed and ground in an agate mortar. Infrared measurement was carried out in the transmission mode, in which the infrared beam directly passes through the sample, 32 scans for each sample have been performed. F-Fisher's test, by Excel software, was conducted on the 1801 wavelengths. Raw transmission spectra were imported in the WinISI II vers.1.5 software (Infrasoft International, Port Matilda, PA, USA) and chemometrics was performed in two steps. By first a stepwise selection procedure identified 6 spectral bands particularly relevant into discriminative purposes. By second a leave-one-out procedure, carried on by StatBox v.6.5 (Grimmer Logiciels, Paris), and validated each specimen traceability. This software was also used to delineate the relationships between the six bands, using a Cluster Hierarchical Ascendant (CHA) procedure.

RESULTS

The transmittance values were constantly inferior in the HM (-15%) (Figure 1). This must be considered as sign of a richer content of constituents. All along the spectra, from 4000 to 400 cm-1, the F fisher's test of single wavelength differentiated maximally the two types at 402 cm-1 ($P=0.23$), and the P was <0.24 in 30 bands (Figure 2). The wavelength selection process clusterized 6 bands (2476, 1596, 1364, 608, 596, 402 cm-1) whose relationships is reported in Figure 3. In particular, the similitude coefficient neighbored 596, 608 and 1364 cm-1 bands, clustered to 402 cm-1, then to 1596 cm-1 while the 2476 cm-1 was most separated.

In a literature examine (2-4, 14-16), tarhana includes principal constituents, as water, carbohydrates, acids, protein and free amino-acids , ash and minerals, salt, fat; but also secondary constituents, as vitamins (thiamine (B1), riboflavine (B2), B12, ascorbic acid (C), niacin (B3), pantothenic (B5), folic acid) and finally microbe agents as lactic acid bacteria. In vibrational spectroscopy, composition of tarhana can be indirectly envisaged by chemical bond, via their vibrational excitation. IR spectral results of home made and commercial types are given in Figure 4 and Figure 5, respectively. Spectral data of all types were summarized in Table 1. In respect to the differential composition of the commercial and home-made tarhana some suggestion arise from some of the bands outlined in Figure 3.

The O-H stretching vibration at about 3430 cm-1 shows the moisture of samples, in Table 1 Most of home made tarhana samples shows higher frequencies, while commercial types have lower frequencies of O-H stretching band, this may be caused by sun-dried (it depends the weather conditions) and vacuum dried/temperatures of oven differences on moisture content, as one of scientists claimed that drying methods in making tarhana can affect the functional properties of tarhana (17). However this band did not revealed significance in traceability. The protein structure of tarhana can be monitored by amide I band (C=O stretching band) at approximately 1650 cm-1 and amide II (N-H deformation band) band at about 1540 cm-1. Some band shifts to lower or higher frequencies, each sample has different recipes while the ingredients of tarhana are almost the same and the quantity of contents differs along with varying the ingredients. The order in which ingredients are added different, waiting and drying conditions are different; all changes make vibrational frequencies shift. The discriminative band at 1596 cm-1 may indicate some difference in the protein profile of the two types. Almost all types of vitamin B share the same structure in their composition. The common functional groups of vitamin B are CH2 and CH3 that were assigned in Table 1. The band appears at about 2926 cm-1 assigned to asymmetrical CH2 stretching mode probably caused one of vitamin complex. And other CH2 and CH3 vibrations certified the vitamins. Presence of riboflavine was predicated by the band at 1240 cm-1 (18). This band which is the characteristic band of riboflavine had been determined between the regions at 1239-1247 cm-1 in all samples. Bands observed at around 1420 cm-1 and 1340 cm-1 are characteristics bands of vitamin B3 (19). The discriminative band at 1364 cm-1 may indicate some difference in the vitamin B3 content of the two types. The characteristic vibrational frequencies of ascorbic acid have been observed by other scientists (20-24). The bands observed at 1739-1745 cm-1 in all samples can be assigned as C=O stretching vibrations and the band at 1080 cm-1 can be attributed to C-O-C stretching vibration. These two typical bands supported the idea of validity of ascorbic acid. The peaks determined in the region 990-1027 cm-1 are related to the lactone ring deformation of vitamine C that it indicated before the work (25). The most discriminative band which resides in the range around 608, 596 and mainly at 402 cm-1 may be related to CCC, skeletal vibrations and CCN vibrations, respectively (26). This region is also called Far-IR region which is related to some metal bonds that can not be assigned by only IR interpretations. The Table 2 reports the multiple regression equation which was developed on the six bands. The discriminative equation in calibration featured a R2 0.92 (P.adj 0.83). After full cross-validation the R2 values descended to 0.65, but as it can see in the Figure 6, only 1 sample of CO type was missed as HM.

CONCLUSION

Comparing the commercial and home-made types of tarhana, it is concluded that vibrational frequencies of tarhana are characterized by the same bands for both commercial andhome- made varieties. The main vibrational modes were investigated in this study.

Making tarhana at home is a cultural heritage and now its commercial production and sale are economic inputs. As lifestyle changes traditional foods are viewed not only as nutritious value but also the optimal choice for a healthier life. FTIR is shown to be a powerful analytical tool to draw conclusions about the chemical identification of organic functional groups in tarhana. These organics will be desirable or not can be easily detected by FTIR spectroscopy.

This paper outlines that; traceability of tarhana could be improved by the rapid FTIR technique and incorporated into quality control.

Regional diversity of amounts and types of ingredients, as well as processing techniques, affect chemical compositions and vibrational frequencies shifts. Desirable effects are envisaged by a systematic use of the FTIR spectroscopic techniques.

FTIR spectroscopic techniques require only 2 minutes for each sample analyzed. Furthermore, this technique needs less solvents and toxic reagents than other analytical methods.

In the view of the social dimension, women in Turkey will continue to make tarhana at their home, unaware of the vibrational frequencies of tarhana. But this precious food could be sold all of over the world, and the commercial varieties should be the best quality and quality control can be handled by lots of different methods.

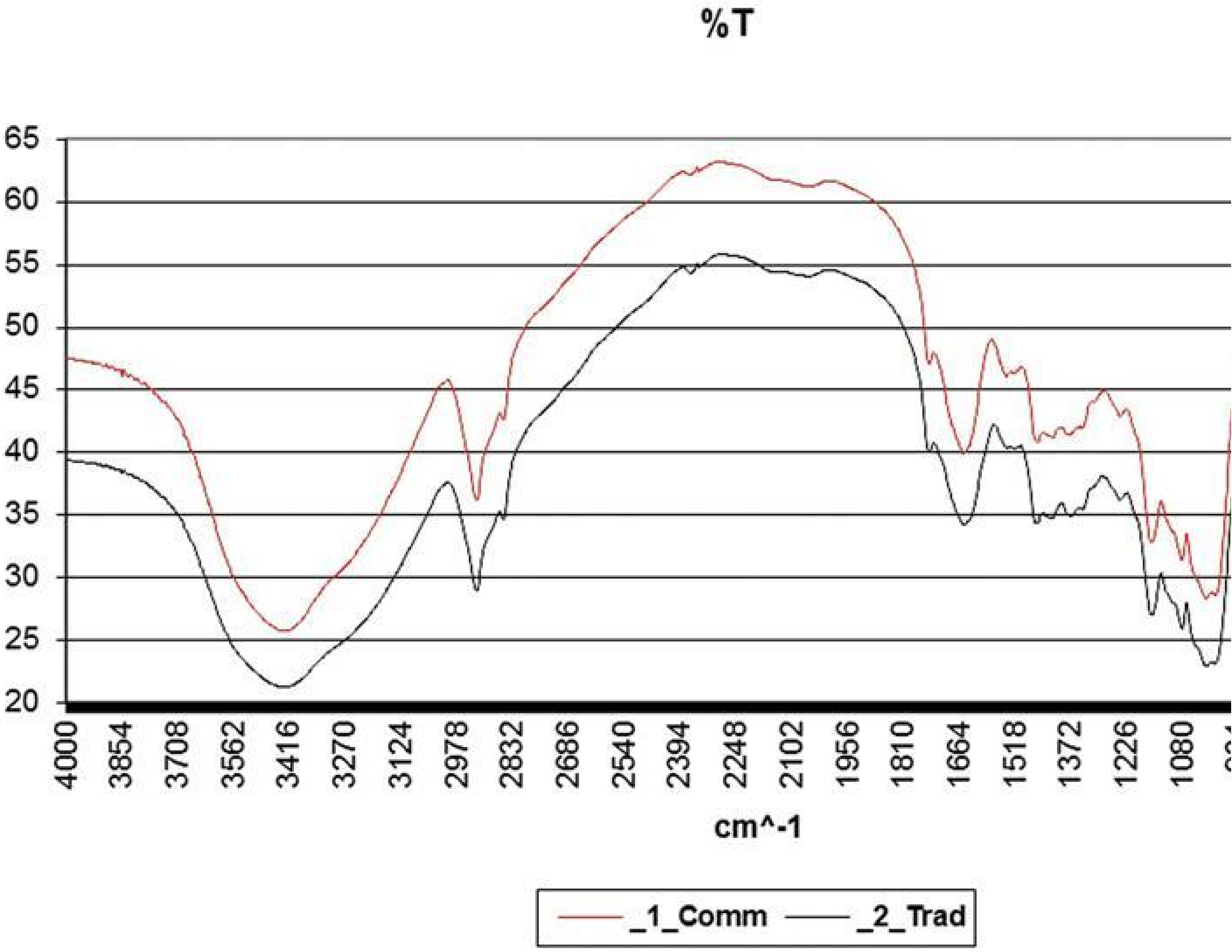


Figure 1. Average Transmittance curves of the commercial (red line) and home-made or tradional (black line) types of tarhana .

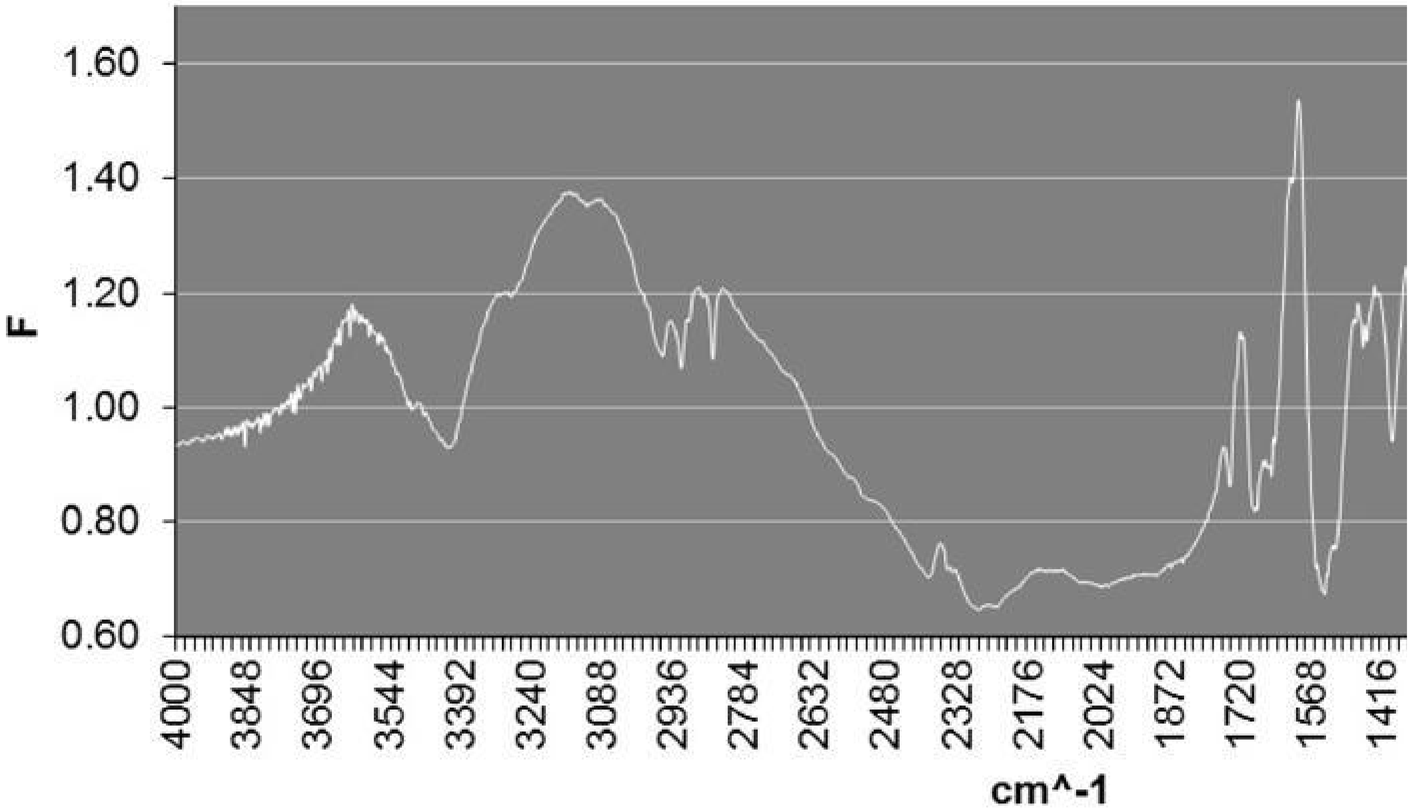


Figure 2. F-Fisher's test values from 4000 to 400 cm-1 wavelengths which differentiated the Commercial and Home-Made tarhana.

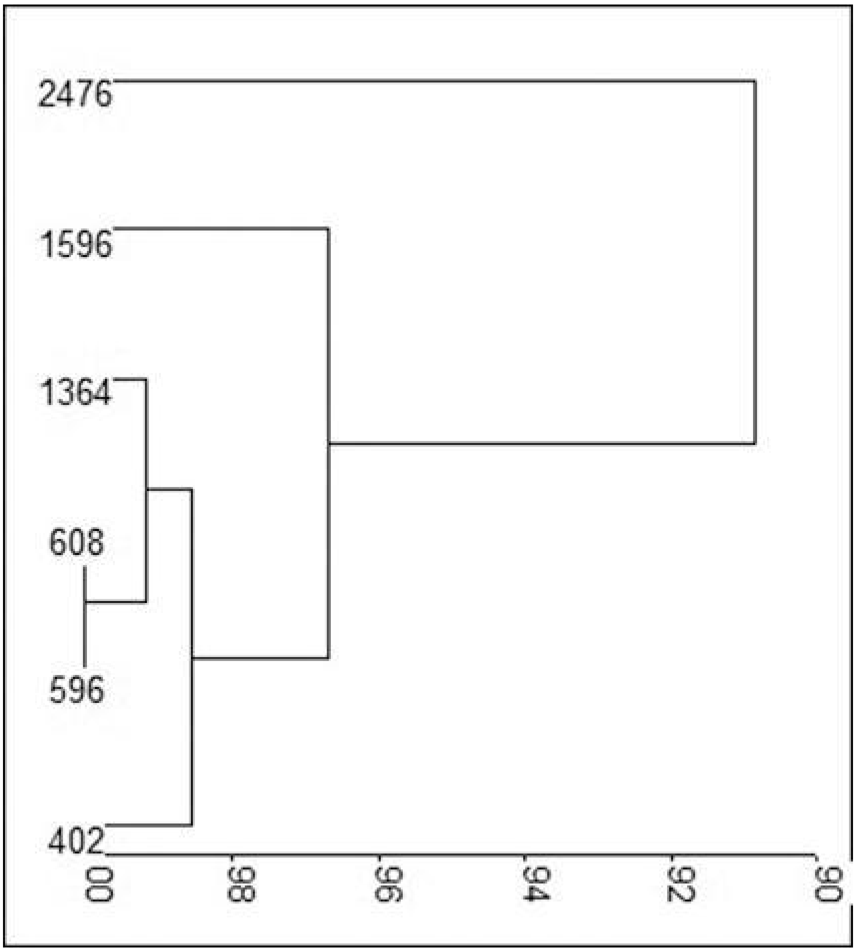
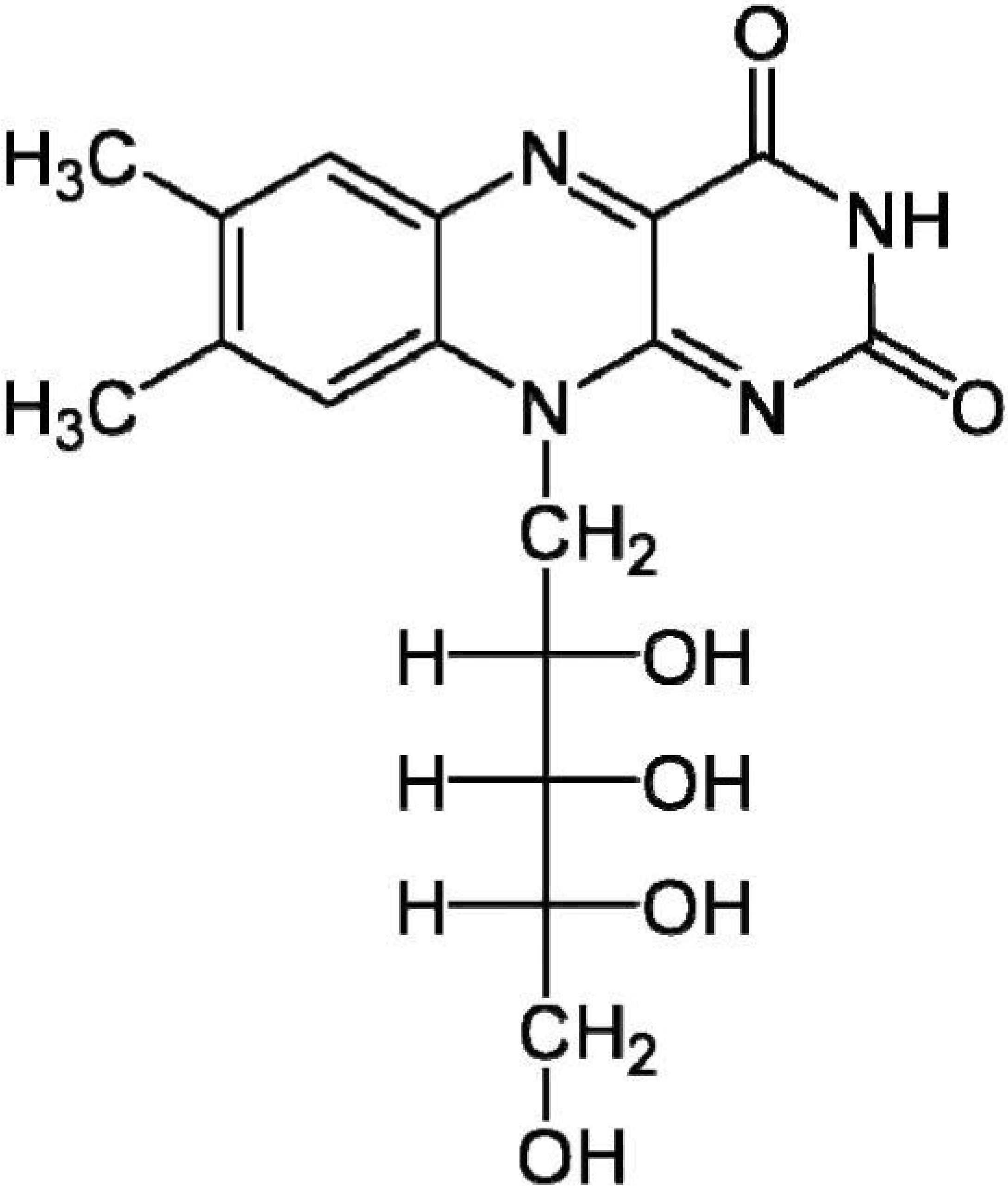


Figure 3. Cluster Hierarchical Analysis of the six most relevant wavelengths, which discriminate the commercial and home-made tarhana. Abscises: Pearson correlation difference.



Riboflavine

Figure 4. Molecular structures of fundamental components in tarhana

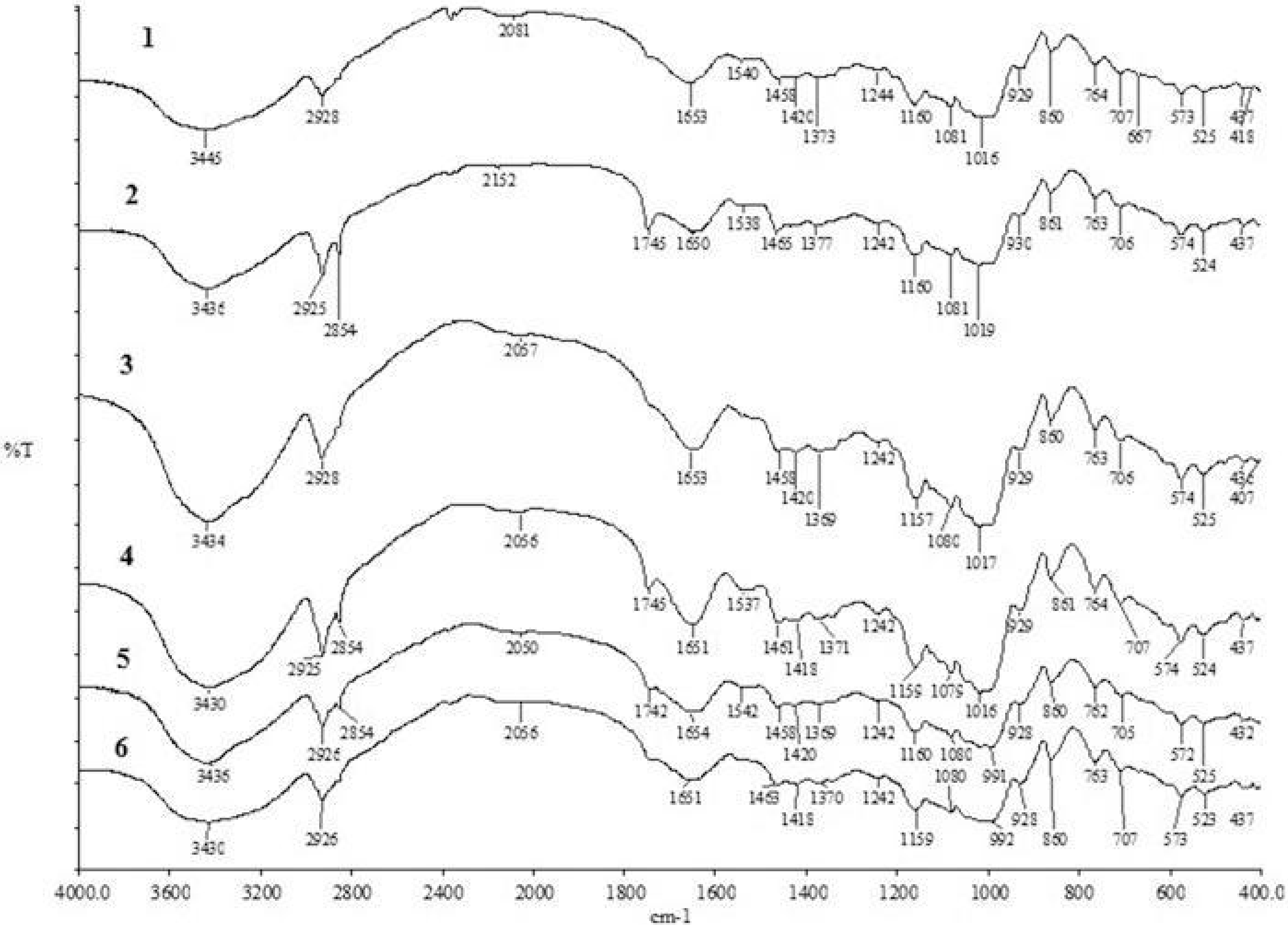


Figure 5. IR spectra of home made tarhana (hm types)

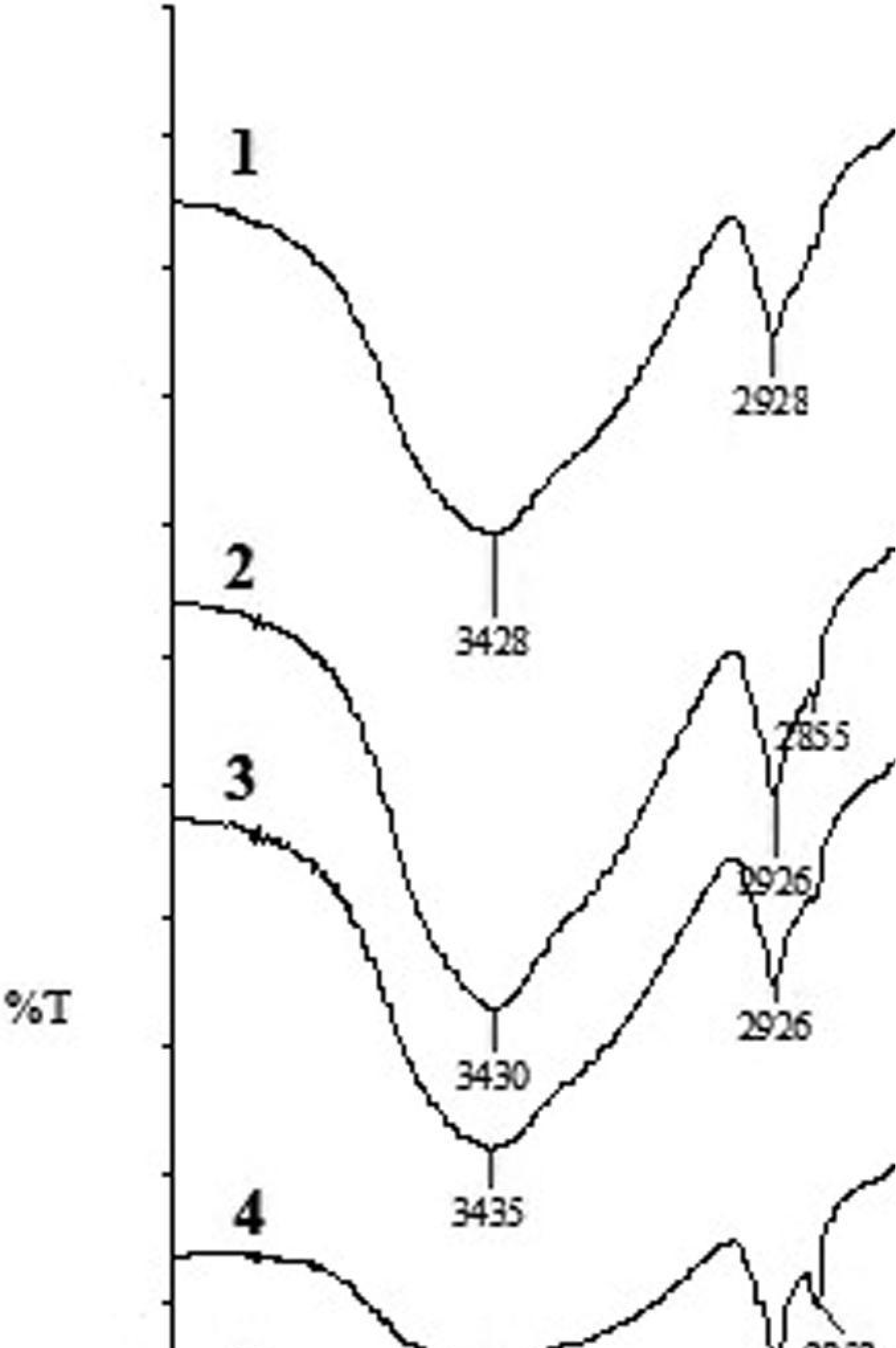

%T
1
2928
3428
2
2855
2926
3430
3
2926
3435
4

Figure 6. IR spectra of commercial type tarhana (com types)

Commercial types samples						Assigments		
1-com	2-com	3-com	4-com	5-com	6-com		1-hm	2-h
3428	3430	3435	3435	3428	3435	O-H str.	3445	34
2928	2926	2926	2922	2926	2928	Asy. CH_2 str.	2928	29
			2852	2854	2857	Sym.CH_2 str.	2857	28
2056				2057	2056	C-H bend.	2081	
	1739	1739	1744	1745	1742	C=O str.	1742	17
1651	1653	1654	1652	1646	1654	Amide I (C=O) str.	1653	16
	1540	1541	1539	1540	1541	Amide II (N-H def.and C=N str.)		15
1458	1457	1458	1465	1458	1459	C-H bend. of CH_2 ve CH_3	1458	14
1418					1420	C-H def.	1423	
1372					1370	C-H in plane bend.	1373	
	1342					C-H in plane bend.		13
1243	1243	1241	1243	1244	1243	(C-N) str. Or C-N-H str.	1247	12
1159	1158	1160	1162	1161	1159	C-O str.	1160	11
1080	1080	1080	1082	1078	1080	C-O-Cstr. C-O-H bend.	1081	10
1018	1019	1018	1018	1020	1018	C-O bend.	1016	10
995		993	991	990	993	Out of plane C-H bend.	995	99
930	931	931	931		931	Out of plane C-H bend.	929	93
860	860	860	860	860	860	Out of plane C-H bend.	860	86
763	763	763	764	763	763	Out of plane C-H bend.	764	76
706	706	705	707	704	707	Ring def.	707	70
606	604	609	606		609	İn plane CCC def.	612	60
574	573	573	573	574	574	Skeletal str. of in plane def.	573	57
526	525	524	525	527	525	Out of plane CCC def.	525	52
					475	Out of plane ring def.		47
437	434	434	434	434	434	Ring def.		43

Table 1: IR spectral data of tarhana samples (in cm-1)
str= stretching, bend.= bending, def.= deformation, asy.= asymmetric, sym.= symmetric,

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