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Study on Dissociation of Nano Bamboo Extractives

Abstract. *Bamboo, which is considered one of the best renewable resources on the planet, has widely been used. However, the extractives has a serious influence on bamboo processing, pulping and papermaking. Therefore, bamboo extractives of Phyllostachys heterocycla was done in the different solution, and studied by GC-MS. The results showed that the optimal extracting time of ethanol extraction, benzene/ethanol extraction and acetic ether extraction reached the largest leaching rate of bamboo extractives was 8h, 7h and 6h, respectively. The bamboo benzene/alcohol extractives had a main retention time between 30-40 min and contained 55 components. The acetic ether extractives had a main retention time between 20-40 min and contain 46 components. The ethanol extractives had a main retention time below 40 min and contain 28 components,.*

Streszczenie. *W artykule przedstawiono wyniki analiz drewna bambusowego, pod względem wpływu jego ekstraktów na proces przetwórczy. W badaniu wykorzystano metodę GC-MS, na podstawie której wyznaczono szybkość wydobycia poszczególnych substancji. Dodatkowo określono skład każdego z wydobytych ekstraktów. (**Badania wydzielania ekstraktów z drewna bambusowego**).*

Keywords: Bamboo extractives, *Phyllostachys heterocycla*, GC-MS
Słowa kluczowe: ekstrakty z bambusa, *Phyllostachys heterocycla,* GC-MS.

1. Introduction

Bamboo is one of the fast growing planet in the world, and also is one of the fast-growing forest plants in tropical and subtropical regions. And *Phyllostachys heterocycla* is the most dominant among a variety of bamboo species. Comparing with wood, bamboo has many excellent characteristics, such as rapid growth, high yield, high strength, high toughness, and high hardness [1]. Bamboo is commonly used as a food source, and also used to make a variety of household goods such as furniture, dinnerware, sporting goods, jewelry and handbags [2]. So bamboo has been an important and economic tree especially for poor people and poor family.

Bamboo biomass contains cellulose, hemi-cellulose, ligin, and extractives. And the extractives is the minor ingredient of bamboo. But the extractives has a serious influence on bamboo processing, pulping and papermaking [3,4]. Especially, the extractives easily caused bamboo moldy. Researches on bamboo extractives have mostly focused on shoots, roots, and leaves for the bioactive components with antioxidant activity and antimicrobial activity[5-8]. The extractives leachded out of bamboo as nano particles[9], and it was difficult to clearly reveal the leaching characteristics. Therefore, bamboo extractives of *Phyllostachys heterocycla* was done in the different solution, and studied by GC-MS.

2. Materials and Methods

2.1. Test Material

The 4-year-old *Phyllostachys heterocycla,* which lived in Xiangtan City, Hunan province China, was provided by Hengdun Limited Company in Hunan. The sample bamboo were dried to absolute dry in 105°C. About 40-60 mesh powder was sieved out using AS200 Sieving Instrument(Made in America). The qualitative filter paper and pure cotton extracted by benzene/alcohol solution for 24h. Benzene, ethanol, acetic ether(chromatographic grade) were prepared for the subsequent experiments. Benzene/alcohol solution is a mixture of benzene and ethanol and volume ratio was 1:2.

2.2. Test Methods

Weighed 30 pieces of wood powders, each was about 2g(0.1mg accuracy) and finally parceled by using the quantitative filter paper and tied by using cotton thread, and signed. Extraction was carried out in 150ml solution by the Soxhlet extraction apparatus. Samples were removed at different times(4h, 5h, 6h, 7h, and 8h), Solvents were ethanol, acetic ether and benzene/ethanol solution(Vethanol/Vbenzene=2), respectively. Parallel sample number was 2. After extraction, samples were baked to be absolute dried and weighed. Finally, the leaching rate of bamboo extractives was calculated.

GC/MS combined condition: Gas Chromatography conditions of QP2010 gas chromatography/mass spectrometry apparatus of Japan-Shimadzu company: chromatography column for DB-1(30mx0.25mm) elastic quartz capillary tube column, carrier gas for nitrogen, injection port temperature for 250°C, Sampling: split injection, split ratio: 10:1, column flow: 1ml/min, gas: He, column oven temperature conditions: 50°C(keeping 3min), then heating at 8 °C /min up to 200°C, and at 5°C /min up to 300°C(keeping 10min).Mass spectrometry conditions: ionization methods for EI, electronic energy for 70ev, voltage multiplier gain for 350V, flow speed for 1mL/min, scan quality range for 35~335AMU(m/z).

3. Results and Analysis

3.1. Dissolution law of bamboo extractives

The leaching rate of bamboo extractives was showed in Table1.

Table 1. The results leaching rate of bamboo extractives [%]

Extraction time [h]	Benzene/alcohol Extraction	Ethanol Extraction	Acetic ether Extraction
4	9.7	7.4	9.9
5	9.8	7.8	10.1
6	10.1	8.2	10.3
7	10.4	8.3	9.8
8	11.3	8.5	9.6

The leaching rate trend of bamboo extractives in different solvents was described in Table 1. It was observed that during alcohol extraction, the leaching rate of wood extractives increased, and reached the maximum (8.5%) when extraction time was 8h. During acetic ether extraction, the leaching rate of bamboo extractives first increased, then decreased, and reached the maximum (10.3%) when extraction time was 6h. During benzene/alcohol extraction, the leaching rate of bamboo extractives first increased, then decreased, and reached the maximum (10.4%) when extraction time was 7h. And bamboo was successively extracted in benzene/alcohol, alcohol and acetic ether for 7h, 8h and 6h, , respectively. the leaching rate of alcohol extraction, acetic ether extraction, and benzene/alcohol extraction were 9.1%, 8.8%, and 10.6%, respectively.

3.2. GC/MS Analysis of Bamboo Extractives

During ethanol - acetic ether- benzene/alcohol sequential extraction, three solvent extractives (ethanol extractives, acetic ether extractives, benzene/alcohol

extractives) were obtained respectively. The total ion chromatograms of three solvent extractives by GC/MS were shown in Fig.1, Fig.2 and Fig.3, respectively. Relative content of each component was counted by area normalization. Analyzing the MS data, the NIST standard MS map by computer, open-published books and papers, then components and their contents were identified .

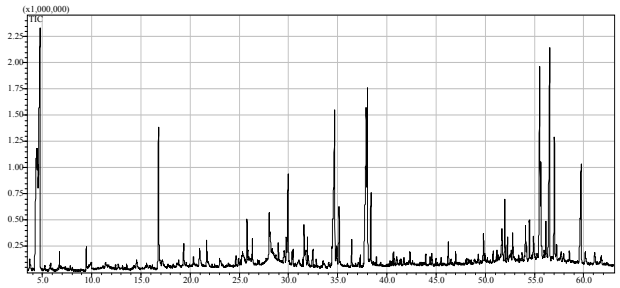

Fig.1. The total lon chromatograms of benzene/ethanol extractives

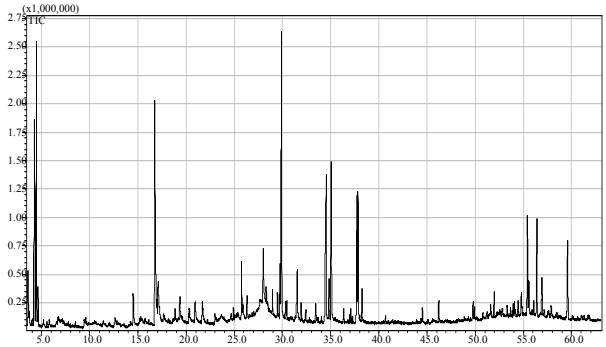

Fig.2. The total lon chromatograms of ethanol extractives

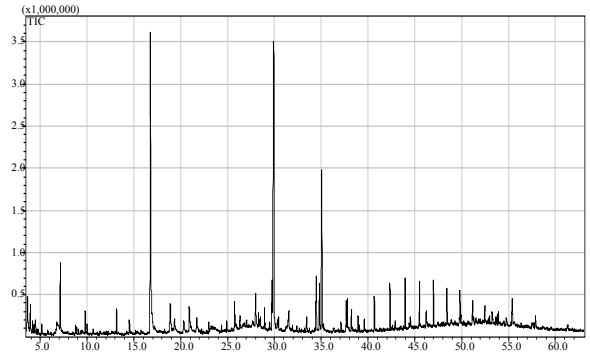

Fig.3. The total lon chromatograms of acetic ether extractives

Table 2. Analytical Results of bamboo benzene/ethanol extractives

No.	R.T. [min]	P.K.. [%]	Corresponding material
1	4.423	8.73	2,3-Glycol Butyl
2	4.758	11.38	2,3-Glycol Butyl
3	6.713	0.25	Cyclohexyl Alcohol
4	9.451	0.35	Phenol
5	13.132	0.03	N-Dodecane
6	13.577	0.07	Benzene Ethanol
7	14.583	0.16	2,3-II hydrogen -3,5-II hydroxyl -6-methyl -4-ketone-4 hydrogen effects furans
8	16.804	3.88	2,3-II hydrogen benzene and furan
9	19.341	0.37	4-vinyl base -2-methyl oxygen base phenol
10	20.343	0.14	2,6-II methyl oxygen base phenol
11	20.964	0.52	4-hydroxyl benzene formaldehyde
12	21.696	0.49	vanillin
13	22.994	0.10	2-methyl oxygen base -4-propylene base phenol
14	24.649	0.16	4-hydroxyl -3-methyl oxygen base benzoic acid methyl ester
15	28.044	1.03	4-hydroxyl -3,5-II methyl oxygen base benzene formaldehyde
16	28.965	0.27	2,6-II methyl oxygen base -4-(2-propylene base)-phenol
17	29.556	0.52	4-hydroxyl -3-methyl oxygen base benzene acetate methyl ester
18	29.965	2.75	4-((1E) -3-hydroxyl -1-propylene base) -2-methyl oxygen base phenol
19	30.371	0.27	Myristic acid
20	30.468	0.27	4-hydroxyl -3,5-II methyl oxygen base benzene methyl n hydrazine
21	32.477	0.44	15 acid
22	34.706	7.66	Palmitic acid
23	36.433	0.46	Daturic acid
24	37.277	0.17	Phytol
25	37.915	7.15	Llinoleic acid
26	38.025	4.50	Oleic acid
27	38.376	1.31	Stearic acid
28	38.938	0.12	Nonadecansaure
29	40.683	0.21	Tricosane
30	41.741	0.07	Iicosanoic acid
31	42.347	0.15	Tetracosane
32	43.951	0.14	Pentacosane
33	45.400	0.02	Docosanoic acid
34	45.497	0.10	N-Hexacosane
35	46.500	0.08	Tricosanic acid
36	46.994	0.17	Heptacosane
37	47.977	0.07	Tetracosanic acid
38	48.113	0.08	Erucamide
39	48.437	0.05	N-Octacosane
40	48.584	0.05	Squalene
41	52.777	0.51	Vitamin E
42	54.084	0.96	Ergost-5-en-3-ol, (3.beta.)-
43	54.489	0.85	Stigmasterol
44	55.547	6.03	γ- sitosterol
45	55.644	2.24	4,4,6a,6b,8a,11,11,14b-Octamethyl-1,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-octadecahydro-2H-picen-3-one
46	59.721	3.72	Phyllanthus niruri Linn

Table 3. Analytical results of bamboo ethanol extractives

No.	R.T. [min]	P.K.. [%]	Corresponding material
1	3.603	1.27	Pyridine
2	4.275	6.32	2,3-Butanediol
3	4.486	8.37	2,3-Butanediol
4	8.506	0.07	1,1-Dimethoxy -3-Methyl-Butane
5	14.519	1.11	2,3- Dihydro-3,5- Dihydroxyl -6- Methyl -4-Ketone –Tetrahydropyran
6	16.755	9.29	2,3- Dihydrobenzofuran
7	17.093	2.55	5- Hydroxymethyl -2-Carbonfuran
8	18.847	0.21	2- Undecanone
9	19.339	0.65	2- Methoxy -4- Yinylphenol
10	20.343	0.38	2,6- Dimethyoxy Phenyl Hydroxide
11	20.924	0.72	4- Hydroxybenzaldehyde
12	21.68	0.53	Vanillin
13	22.994	0.19	2- Methoxy -4- Allylhydroxy Benzene
14	29.49	0.73	4- Hydroxyl -3- Methyl Phenylacetate
15	29.894	9.75	4-((1E)-3- Hydroxyl -1- Allyl group）-2-Methoxyphenol
16	30.442	0.40	4- Hydroxyl -3,5- Dimethoxy Benzoyl Hydrazine
17	33.743	0.07	14- Methyl - pentadecanoic acid methyl ester
18	34.525	4.05	Palmitic acid
19	36.365	0.30	daturic acid
20	36.964	0.16	9,12- Mandenol
21	37.100	0.27	methyl elaidate
22	37.270	0.13	Reaction Phytol
23	37.730	3.88	linoleic acid
24	37.842	3.34	oleic acid
25	38.246	0.72	stearic acid
26	54.064	0.47	rapeseed sterols
27	55.570	1.04	4,4,6a,6b,8a,11,11,14b- octamethyl -1,4,4a,5,6,6a,
28	59.596	3.36	Phyllanthus niruri Linn 6b,7,8,8a,9,10,11,12,12a, 14,14a,14b-octadecahydro-2H-picen-3-one

Table 4. Analytical results of bamboo acetic ether extractives

No.	R.T. [min]	P.K.. [%]	Corresponding material
1	3.632	2.52	sec-butyl acetate
2	3.942	1.34	isobutyl acetate
3	4.165	0.25	2,3- butanediol
4	4.357	0.20	2,3- butanediol
5	4.486	0.72	Ethyl butyrate
6	4.782	0.14	butyl acetate
7	7.132	1.75	Ethylene glycol monobutyl ether
8	8.780	0.26	1- ethyl group -3 methylphenyl
9	8.878	0.20	1- ethyl group -4 methylphenyl
10	9.044	0.15	1,3.5- Trimethylbenzene
11	9.306	0.09	1- ethyl group -2- methylphenyl
12	9.807	0.58	1,2,4- Trimethylbenzene
13	10.006	0.3	n-Decane
14	10.64	0.13	1,2,3- Trimethylbenzene
15	13.146	0.61	n-dodecane
16	14.503	0.59	2,3- dihydro-3,5- dihydroxyl -6- methyl -4- ketone -4 hydropyran
17	16.766	16.26	2,3- Dihydrobenzofuran
18	18.877	2.25	Isosorbide
19	19.133	0.12	2- hydroxybenzoic acids
20	19.338	0.48	2- methoxy -4- vinylphenol
21	20.333	0.6	Pyrogallol 1,3-dimethyl ether
22	20.907	1.33	4-Hydroxybenzaldehyde
23	22.221	0.09	α- cedrene
24	22.997	0.4	2-methoxy-4-propenylphenol
25	24.357	0.15	butylated hydroxytoluene
26	27.028	0.18	8.beta.H-Cedran-8-ol
27	28.487	0.27	Cycl-tetradecane
28	29.003	0.1	Heptadecane
29	29.476	0.34	4- hydroxyl -3ethyl methyl acetate
30	29.925	17.02	4-((1E)-3- hydroxyl -1- Allyl group）- 2- methoxyphenol
31	30.304	0.19	Myristic acid
32	30.446	0.39	4- hydroxyl -3,5- dimethoxybenzoic acid hydrazide
33	31.18	0.05	n-octadecane
34	32.392	0.17	1,2-Benzendicarboxylic acid bis [2-methylpropyl] ester
35	34.308	0.08	di-n-butyl phthalate
36	34.481	2.93	Palmitic acid
37	35.232	0.2	n-Heneicosane
38	37.668	1.05	linoleic acid
39	37.793	1	oleic acid
40	38.228	0.6	stearic acid
41	38.934	0.45	Docosane
42	39.066	0.2	2-hydroxy-propanoic aci hexadecyl ester
43	39.595	0.36	2-Naphthalenamine, N-phenyl-
44	40.675	1.01	tricosane
45	42.342	1.32	Tetracosane
46	43.953	1.41	pentacosane
47	44.382	0.14	CIOP
48	45.499	1.26	n-Hexacosane
49	46.988	1.26	Heptacosane
50	48.434	1.05	n-Octacosane
51	49.822	1.03	N-nonacosane
52	51.166	0.74	Triacontane
53	52.47	0.55	Hentriantane
54	53.767	0.32	dotriacontane
55	55.261	0.1	Tritriacontane

According to GC/MS result, 55 components were identified from bamboo benzene/alcohol extractives. The result showed that the main components were 2,3-butanediol(20.11%), palmitic acid(7.66%), linoleic acid(7.15%), γ- sitosterol(6.03%), oleic acid(4.5%), 2,3-dihydrobenzofuran(3.88%), phyllanthus niruri linn(3.72%), 4-((1e)-3-hydroxyl-1- propylene base)-2-methyl oxygen base phenol(2.75%), stearic acid(1.31%), vanillin(0.52%), and so on,

According to GC/MS result, 28 components were identified from bamboo alcohol extractives. The result showed that the main components were 2,3-butanediol(14.69%), 4-((1E)-3-hydroxyl-1-propylene base)-2-methyl oxygen base phenol(9.75%), 2,3- dihydro-benzofuran(9.29%), palmitic acid(4.05%), linoleic acid (3.88%), phyllanthus niruri linn(3.36%), oleic acid(3.34%), 5-hydroxymethyl-2-carbonfuran(2.55%), pyridine(1.27%), vanillin (0.53%), and so on.

According to GC/MS result, 46 components were identified from bamboo acetic ether extractives. The result showed that the main components were 4-((1E)-3-hydroxyl-1-propylene base)-2-methyl oxygen base phenol(17.02%), 2,3-dihydrobenzofuran(16.26%), palmitic acid(2.93%), sec-butyl acetate(2.52%), isosorbide(2.25%), ethylene glycol monobutyl ether(1.75%), and so on.

3.3. Chemical distribution characteristic of bamboo extractives

The richest components of benzene/alcohol extractives were 2, 3-butanediol (20.11%); and there were 11 kinds of water-soluble compounds (33.32% of the total peak area), 12 kinds of acid compounds (21.68%), 2 kinds of resin compounds (0.68%), and 7 kinds of hydrocarbons (0.85%), 13 other substances (11.70%).

The richest components of acetic ether extractives were 4-((1E)-3- hydroxyl-1-propylene base)-2-methyl oxygen base phenol (17.02%); and there were 4 kinds of water-soluble compounds (5.78%), 6 kinds of acid compounds (5.89%), 9 kinds of resin compounds (5.65%), 18 kinds of hydrocarbons (12.03%), 13 other substances (19.43%).

The richest components of ethanol extractives were 2,3-butanediol(14.69%); and there were 7 kinds of water-soluble compounds (20.11%), 5 kinds of acid compounds (12.29%), 4 kinds of resin compounds (1.23%), 1 kinds of hydrocarbons (0.07%), 10 other substances (26.63%).

The retention time of each solvent extractives of bamboo showed a particular rule. The distribution characteristic of bamboo extractives was listed in Table 5.

Table 5. Distribution characteristic of bamboo extractives

Retention time [min]	benzene/alcohol extractives	alcohol extractives	acetic ether extractives
＜10	20.71	16.03	8.20
＜20	4.51	13.81	20.74
＜30	5.98	12.30	20.48
＜40	22.35	13.32	7.67
＜50	1.19	0	8.48
＜60	14.31	4.87	1.71

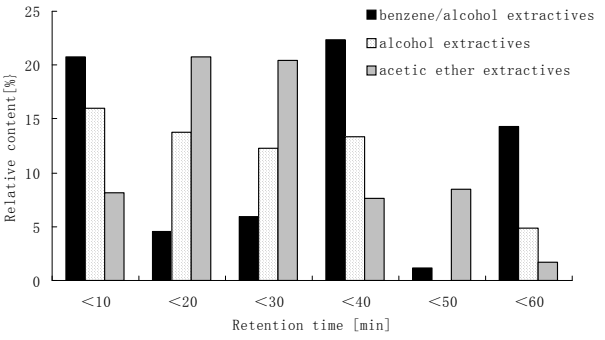

Fig.4. The relationships between retention time and relative content

The bamboo ethanol extractives had a main retention time <40 min, which accounts for 55.46% of the total relative content; however, the relative content of above 40 min retention time was only 4.87%. The acetic ether extractives had a main retention time below 20-40min, the relative content of below 20 min retention time was 41.22%.

The benzene/ethanol extractives had a main retention time between 30-40 min, which accounts for 22.35% of the total relative content, but the other retention time displayed a wide distribution of components and their relative contents were very few (Fig. 4).

4. Conclusions

During single extraction, among three extracting solvents including ethanol, benzene/ethanol and acetic ether, the optimal extracting time to reach the largest leaching rate of bamboo extractives was 8h, 7h and 6h, respectively. During the sequential extraction, each sequential extraction displayed gradually increased leaching rate, whose total leaching volume was larger than that of single extraction.

The bamboo benzene/alcohol extractives had a main retention time between 30-40 min and contain 55 components, especially including 2,3-butanediol(20.11%). The acetic ether extractives had a main retention time between 20-40 min and contain 46 components, especially including 4-((1E)-3- hydroxyl-1-propylene base)-2-methyl oxygen base phenol(17.02%). The ethanol extractives had a main retention time below 40 min and contain 28 components, especially including 2,3- butanediol(14.69%).

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