Simulation Experiments of Distillers of Han Dynasty

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Research article

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Abstract

One set of implements was unearthed from Haihunhou Tomb and Zhangjiabao Tomb respectively. It is speculated that they may be ancient stills. In order to verify their distillation properties and efficiency,We make two imitations referring to the two unearthed sleeves and simulation experiments were conducted on distilled spirits and distilled flower dew. The distillated product is analyzed with the help of alcoholometer and GC-MS. The results showed that the distillers could produce higher degree of liquor and extract flower dew effectively. The distillation effect of unearthed objects is better than that of imitations. They were undoubtedly distillers with good distillation effect. The properties of two stills of Han Dynasty were confirmed by the simulation experiment.

1. Introduction

The tomb of Zhang jiabao (9–23 AD), Xi'an, excavated in 2007, and the tomb of Hai hunhou(92 – 59 BC), Nanchang, Jiangxi, excavated in 2016.the two tomb owners were high-grade nobles. Two tombs respectively unearthed a set of utensils(Fig. 1 and Fig. 2). The objects are made of bronze and consist of three parts, the bottom is the kettle, the middle is the cylinder, and the top is the cover. These two nested artifacts were supposed to be distillers.

The shape of Hai hunhou's artifacts is slightly larger,with the overall height of 132cm and the outer cylinder diameter of 53.4cm. Zhangjiabao's artifacts is smaller, the overall height of the whole device is about 45cm, the over height of the cylinder is 35cm, the diameter of cylinder is 23cm. Referring to the specific size and structure of these two unearthed objects [1] [2],two imitations were made with white iron sheet and stainless steel.The size of the imitation of the Zhangjiabao's artifacts is close to the original, and the size of imitation of the Haihunhou's artifacts is half of the original. For the sake of description, respectively called imitations of Zhangjiabao (Fig. 3) and Haihunhou (Fig. 4) artifacts for A and B.

In ancient China, the distiller had the function of distilling liquor and flower, practicing alchemy and extracting medicine. Therefore, mash, fermented grains and petals were chose as the steaming materials and the distillation experiments were carried out with imitations.

2. Materials And Apparatus

2.1 Raw materials and Reagents

Raw materials

rice, Kunming black magic rose (Chinese rose), distiller's yeast.

Reagents

dichloromethane, anhydrous ethanol, anhydrous sodium sulfate, sodium chloride, all of them are analytical pure.

2.2 Method

The degree of alcohol obtained by distillation was measured by hand-held refractometer alcohol concentration meter (Wuqiang Lingxin instrument Co., Ltd, Hebei, China). The alcohol meter is calibrated with known white spirit before use.

GCMS-Thermo DSQ Ⅱ (Thermo Fisher Scientific, America),used for qualitative and quantitative analysis of the components of flower dew.

GC-MS conditions: *Gas chromatography conditions*: equipped with capillary column HP-5, length (30m ×0.25mm ×0.25μm).The initial column temperature was 50°C for 3min,and it was raised to 200°C at 2°C/min. Then it was raised to 280°C at 10°C/min for 10min.Helium as carrier gas, injection port temperature was 250°C, split ratio was 10:1, column flow rate was 1.0 mL/min. *Mass spectrometry conditions*: Electron bombardment ion (EI) source is used as ionization mode. The monitoring method is full scanning. The ionization energy is 70eV.The ion source temperature is 250°C. The interface temperature is 250°C. The scanning range is 33–500.

Qualitative analysis

the mass spectra were identified by NIST and Wiley Software and the relative content was calculated by peak area normalization method.

2.3 Experiments on Distilling Liquor

There is a grate at the bottom of the cylinder of two unearthed artifacts, which suggests that the two can be distilled in water or above water. The experiments of distillation have been carried out with A and B. The induction cooker was used as heating device.

A: Water distillation experiment was carried out. 800g of rice was taken as raw material, cooked, mixed with the distiller's yeast, and then semi-liquid fermentation was carried out, finally semi-liquid and semi-solid mash was obtained [3]. The mash was placed in the kettle, which occupies half of its capacity. Three parts including kettle, cylinder and cover were tightly fitted. Figure 5 is the sketch map of water distillation of A. Put cooling water into the upper plate of the cover, connect the flow port with the bottle with a rubber hose. Considering the wine speed and bottle volume, replace the bottle every 4 minutes or 8 minutes. Measure the volume and degree of the alcohol and calculate the speed of the wine (Table.1).

The experiment of distillation on water was carried out. 250g rice was weighed, cooked and mixed with the distiller's yeast, 600g fermented grains are obtained by solid state fermentation. 600g solid fermented grains was put on the grate, add water to two-thirds of the kettle. Three parts were closely combined as the sketch map (Fig. 6). The measurement results of liquor are shown in Table.2.

B: Water distillation experiment was carried out. 300g of rice was weighed for semi liquid fermentation to obtain mash, and put the all mash in the kettle, then added some water. The interlayer of the cylinder is filled with water for cooling (see Fig. 7). The measurement results of liquor are shown in Table.3.

The experiment of steam distillation was taken. 175g of rice was prepared into solid fermented grains. Then put all the solid fermented grains on the grate and put water in kettle(Fig. 8). The results are shown in Table.4.

2.4 Experiments on Distilling Rose Dew

The best extraction time of rose dew is 3 ~ 4 hours and the ratio of solid to liquid is 1:4, which can be a reference for next experiments [5]. In order to ensure that the water is not easily evaporated, the liquid in the kettle is heated to boiling with an induction cooker, and then heated with an alcohol lamp to prolong the heating time.

A: The experiment of extracting rose dew by water distillation. Weighed 300g of rose petals, wash with water to remove pesticides and dust on the surface, cut into pieces, put in the kettle, add 1200g of water, heat with alcohol lam for 4 hours. Obtain 190mL of rose dew.

B: Distill and extract rose dew in water. Weighed 500g of rose petals and 2000g of water into the kettle. Using alcohol lamp to heat for 4 hours and got 380mL of rose dew.

A little sodium chloride was added to the rose dew, standing for 10min.Then, used 15mL of dichloromethane to extract the rose dew, combined the organic, added a little anhydrous sodium sulfate, standing for 12 hours, two samples were injected through the membrane. The volatile components of the rose dew were analyzed by GC-MS.

3. Results And Discussions

3.1 Results and Discussions of Experiments on Distilling Liquor

The measurement results of the degree, volume and speed of the liquor are shown as the follow tables.

Table.1 The result of water distillation of A

Time interval(min)	4	4	4	8	8	8	8	8
Volume(mL)	120	140	120	120	156	138	98	46
Degrees(vol)	25	28	43	50	38	10	5	3
Speed(mL/s)	30	35	30	15	20	18	12	6

Table.2 The result of steam distillation of A

Time interval（min）	Volume(mL)	Degrees(vol)	Speed(mL/s)
10	60	45	6
10	55	42	5.5
10	109	14	10.9

It can be seen from the Table.1 that the volume, degree and speed of the first and middle stages are the best. The degree and speed decrease significantly in the last stages. From the Table.2, we can know that the highest degree of liquor that is 45 degrees, which belong to the first stage. And then the degree gradually decreased.

As a general rule the degree of head liquor is often the highest in the initial stages during the distillation. Table 1 shows that head liquor’s degree is slightly lower. It is speculated that the firepower of the induction cooker is so larger that the liquid evaporation in the kettle speed up, and the cooling water was not replaced in time.

ffect of A is no And the area and the temperature of the cooling device can’t guarantee the timely condensation of alcohol vapor. Therefore, the power of the induction cooker was adjusted in the following experiments on distilling liquor. Large fire was used at the beginning and the end of the experiment, and small fire was used when the condensate flowed out.

Compared with water distillation and steam distillation of A, if the low tail liquor was not included, In the water distillation experiment, consumed 800g of raw, produced 396 mL liquor, which exclude the first section and the last section distilling liquor with low degree. The liquor yield is 49.5%, and the average degree of liquor is 43 degrees. In the steam distillation experiment, consumed 250g of rice, obtained liquor 115 mL, the liquor yield was 46%, and the average degree of liquor is 43.6 degrees. It can be seen that the yield of alcohol and alcohol degree are almost the same whether distilled in water or distilled on water. The distillation eless than the distiller in modern folk workshops. The results show that A can distill liquor effectively, and it is undoubtedly a distiller.

Table.3 Volume and degree of liquor by water distillation of B

Time interval(min)	**Volume(mL)**	**Degrees (vol)**	**Speed (mL/s)**
10	20	30	2
10	35	24	3.5
>10	104	15	< 10

Table.4 Volume and degree of liquor by steam distillation of B

Time interval(min)	Volume(mL)	Degrees (vol)	Speed (mL/s)
4	30	22	7.5
4	40	16	10
4	56	10	14
>4	110	5	

It can be seen from table.3 and table.4 that the degree of head liquor by water distillation and steam distillation is the highest, and then gradually decreases. Table.3 shows that in the experiment of water distillation, the highest degree of liquor is 30 degrees. If the liquor below 15 degrees in the end section is not included, the rice is 300g, the volume of the liquor is 55 mL, the liquor yield is 18.3%, and the average degree of liquor is 26.2 degrees. Table.4 shows that distillation on water, the highest alcohol is 22 degrees. If the liquor below 15 degrees is not included, consumed 175g of rice, the volume of the liquor is 70mL, the liquor yield is 40%, the average degree of liquor is 19 degrees. Either way, the liquor yield and alcohol degree are not high. In this regard, we think it is mainly due to the lack of imitation. The experimental results still show that B indeed a distiller.

From the perspective of the structure of the utensil, the cooling area of B is much larger than that of A, but the cooling effect is not as good as that of A, which is related to the position cooling water. The steam of A touches cooling water and then condenses. Although the interlayer of B is filled with water, the main cooling effect is still the cover, which mainly depends on air. It is speculated that if the interlayer changes the cooling water continuously, the cooling effect will be better. In addition, the height and width of B is nearly half of the original, so the area of the cover is 1/4 of the original, the surface area of the inner cylinder wall with water as the cooling medium is 1/4 of the original, which means that the cooling area of B is only 1/4 of the original. It also reflects that the distillation effect of the original should be much better than that of B.

3.2 Results and Discussions of Experiments on Distilling Rose Dew

The total ion flow chromatograms (Fig. 11 and Fig. 12) were obtain from the detection of rose dews of A and B. The corresponding compounds were obtained by computer mass spectrometry library and manual analysis. The volatile aroma components are shown in Table.5 and Table.6.

Table.5 Volatile components in flower dew by water distillation with A by GC-MS

No	RT	SI	RSI	Prob	%Area	Compound name
1	5.94	924	943	77.10	2.83	furfural
2	8.23	866	890	58.15	0.1	Benzene,ethenyl
3	11.53	849	893	62.19	0.12	Benzaldehyde
4	15.93	845	853	41.71	1.17	Benzyl alcohol
5	16.44	875	879	53.21	1.26	Phenylacetaldehyde
6	19.95	716	818	86.97	0.07	Ethyl(2E)-2-cyano-2butenoate
7	20.99	715	860	55.31	0.16	Penylethanol
8	24.46	824	852	87.70	0.15	Silane,cyclohexyldimethoxymethyl-
9	31.29	932	932	92.21	42.37	3,5-Dimethoytoluene
10	32.62	820	839	5.73	0.35	2,7,10-Trimethyldodecane
11	40.36	852	885	60.10	1.14	Benzene,1,3,5-trimethoxy-
12	41.03	790	818	32.89	0.4	α-ionol
13	42.75	862	889	71.87	0.48	Dihydro-β-ionol
14	44.09	805	880	11.40	0.17	2,6,10,-trimethyltridecane
15	45.15	801	835	37.74	0.2	β-ionone
16	46.35	868	886	14.10	0.64	Pentadecane
17	46.92	888	889	50.70	1.55	2,4-Di-tret-buthylphlenol
18	48.75	797	850	5.84	0.46	2,6,11,-trimethydodecane
19	51.42	882	892	42.80	0.32	Diethyl phthalate
20	52.13	878	882	12.82	0.89	Cetane
21	57.62	760	844	12.53	1.42	Heptadecane
22	58.19	833	848	5.86	1.74	2,6,11,15-tetrmethylhexadecane
23	65.92	866	910	5.81	0.59	Phthalic acid,hept-3-yl isobutyly ester
24	68.34	795	865	91.99	0.23	1-Oxaspiro[4.5]deca-6,9-diene-2,8dione,7,9-bis(1,1-dimethylethyl)
25	70.49	890	921	10.46	1.02	Dibutyl phthalate
26	77.26	853	897	25.72	0.58	n-Heneicosane
27	80.52	865	871	7.72	0.93	n-Docosane

No	RT	SI	RSI	Prob	%Area	Compound name
28	82.4	822	832	4.42	1.65	Tricosane
29	83.82	877	891	20.50	2.42	Tetracosane
30	85.96	846	855	5.50	4.07	Hexacosane
31	86.95	860	877	9.94	3.7	Heptacoscane
32	88.08	817	852	7.95	4.02	Octacosane

Table.6 Volatile components in flower dew by water distillation with B by GC-MS

No	RT	SI	RSI	Prob	%Area	Compound name
1	4.25	882	900	52.91	0.43	Toluene
2	5.96	893	906	72.98	1.29	Furfural
3	6.39	837	895	39.58	0.09	2,4-dimethylhept-1-ene
4	7.08	893	917	62.13	0.12	Ethylbenzene
5	7.38	762	856	22.33	0.14	m-Xylene
6	8.25	807	879	37.68	0.1	Styrene
7	11.42	874	895	94.27	0.52	Ethyl cyanoacetate
8	11.54	791	976	50.81	0.19	Benzaldehyde
9	14.19	820	886	23.68	0.23	Decane
10	16.44	852	853	39.66	0.78	Phenylacetaldehyde
11	19.98	734	819	92.60	0.11	Ethyl(2E)-2-cyano-2butenoate
12	24.50	800	852	92.14	0.13	Silane,cyclohexyldimethoxymethyl
13	27.28	902	917	23.83	0.32	Dodecane
14	30.65	838	853	50.57	0.21	Benzene,m-di-tert-butyl
15	31.31	921	921	90.78	65.02	3,5-Dimethoytoluene
16	37.15	777	884	55.72	0.2	Triacetin
17	40.28	854	915	29.56	0.39	Tetradecane
18	40.37	888	906	77.16	0.76	Benzene,1,3,5-trimethoxy
19	40.63	770	909	29.00	0.13	Dodecanal
20	41.05	752	789	26.39	0.23	α-ionol
21	42.75	803	858	53.28	0.13	Dihydro-β-ionol
22	46.37	825	872	14.26	0.65	Pentadecane
23	46.92	900	902	55.61	1.96	2,4-Di-tret-buthylphlenol
24	48.77	772	850	6.66	0.44	2,6,11,15-tetrmethylhexadecane
25	52.14	884	891	19.66	0.88	Cetane
26	57.65	736	825	9.74	1.2	Heptadecane
27	57.99	795	928	5.95	0.63	2,6,10,-trimethyltretradecane
28	65.32	894	907	5.58	0.21	Phthalic acid,hept-3-yl isobutyly ester

No	RT	SI	RSI	Prob	%Area	Compound name
29	68.36	781	851	91.75	0.29	1-Oxaspiro[4.5]deca-6,9-diene-2,8dione,7,9-bis(1,1-dimethylethyl)-
30	69.70	696	750	87.38	0.28	3,5-Bis(1,1dimethylethyl)-4-hydroxybenzenepropanoic acid methyl ester
31	70.5	923	937	0.59	1.6	Dibutyl phthalate
32	87.84	792	831	63.96	1.84	Erucylamide
33	88.5	716	835	41.50	0.27	(E,E,E,E)-squalene

There is no report on the analysis of volatile components in the flower dew of this variety Chinese rose used in experiments, so there is no direct component date for comparison. Due to difference the soil, climate, varieties and hybridization, the emergence of new varieties makes the volatile components of roses in different places is inconsistent. Generally speaking, the main aroma components of European roses are phenyl ethanol and monoterpene, while the main volatile components of Rosa chinensis are 3,5-dimethoxytoluene or 1,3,5-trimethoxybenzene [6].

Comparing the detection results of rose dew distilled by two sets of imitations, rose dew of A identified 32 components, 3,5-dimethoxytoluene, accounting for 42.4%. 33 components were identified of rose dew of B, and the highest relative content was 3,5-dimethoxytoluene (65.0%).The volatile components of two dews are almost the same. The highest relative content is 3,5-dimethoxytoluene, which is the main component of rose essential oil. It can be seen that the two sets of imitations can effectively extract rose dew. The components listed above are very volatile components in flower dew, which require high air tightness and cooler. The analysis results of the flower dew obtained in this experiment show that B can completely retain a variety of aroma components of rose petals. The effect of distillation extraction of rose dew is excellent, and the rose aroma components are complete.

Compared with other kinds of rose dew(Table.7). It can be found that phenylethanol and benzyl alcohol are detected in the rose dew with A, but not detected in the rose dew with B, which indicates that the air tightness of A is better that of B. This is due to the lack of imitation.

Table.7 Comparison of main volatile components in rose dew in literature

	Percentage content(%)								
Compound name	a[7]	b[8]	c[9]	d[10]	e[8]	f[11]	g[11]	h(A)	h(B)
3,5-Dimethoytoluene	50.3	2.55	0.72	12.1	1.05	18.5	11.9	42.4	65.02
Benzene,1,3,5-trimethoxy	-	-	-		-	0.84	3.22	1.14	0.76
Penylethanol	2.76	2.17	-	22.5	30.79	-	-	0.16	-
Benzyl alcohol	-	3.42	-		1.24	-	-	1.17	-
Dihydro-β-ionol	3.42	4.24	-		-	4.61	-	0.48	0.13
Note: a. hybrid Rosa chinensis; b. large rose; Rosa chinensis Jacq; d. fragrant rose; e. raspberry rose; f. Pink Perfume rose; g. orange yellow perfume rose; h. Chinese rose variety used in experiment (Rosa chinensis)									

4. Summary

A and B can not only distill liquor, but also extract flower dew effectively. The yield and degree of liquor obtained by A and B are both high. The flower dew obtained from the experiment of extracting flower dew retains many original aroma components of petals. Different experiments have proved that A and B belong to distiller. The distillation efficiency of the original distiller of Han Dynasty should be far higher than the simulation results of A and B.

The space on the grate of A is relatively small, while the space on the grate and the kettle of B is relatively large. The efficiency of distilling liquor in water with A is better than that on water. There are many kinds of alkanes in flower dew distilled by A. Combined with many information, we tend to think that A is more suitable for distilling in water, especially for distilling Chinese herbal medicines. B is suitable for distilling in water or above water, and its large capacity and unearthed in the wine storehouse indicate that it is more suitable for distilling liquor.

Abbreviations

GC-MS: gas chromatograph-mass spectrometer; A: the imitation of Zhangjiabao’s artifacts; B: the imitation of Haihunhou’s artifacts.

Declarations

Acknowledgements

Not applicable

Founding

Not applicable

Competing interests

Not applicable

Availability of date and materials

The date is available within the article.

Author's contributions

Zhihui Yao provided research projects. Haitong Su designed and completed the experiment. Zhihui Yao and Haitong Su analyzed the date. Haitong Su wrote the manuscript. Zhihui Yao helped perform analysis and edit the manuscript. All authors read and approved the final manuscript.

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Figures

Figure 1

Nested artifacts of Zhangjiabao

Figure 2

Nested artifacts of Haihunhou

Figure 3

The imitation of Zhangjiabao’s artifacts (A)

Figure 4

The imitation of Haihunhou’s artifacts (B)

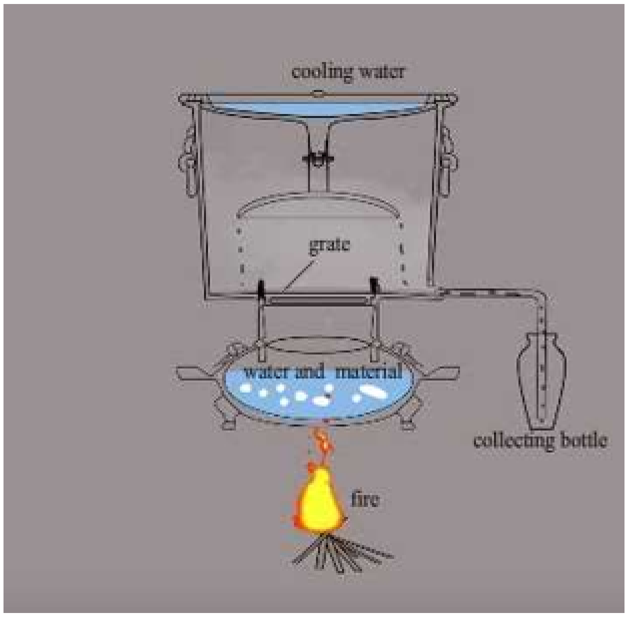

Figure 5

Water distillation of A

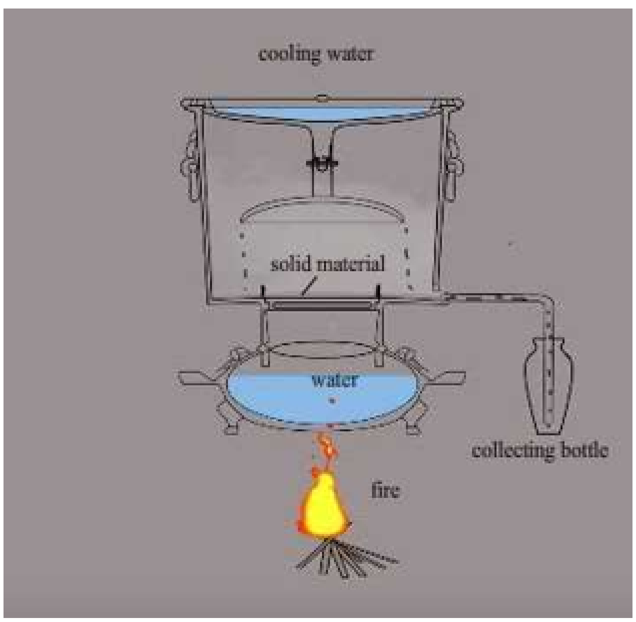

Figure 6

Steam distillation of A

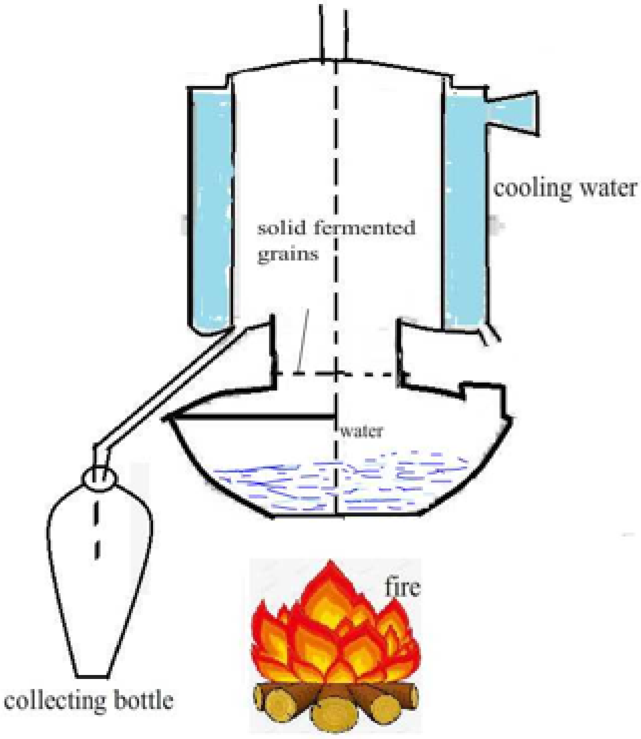

Figure 7

Water distillation of B

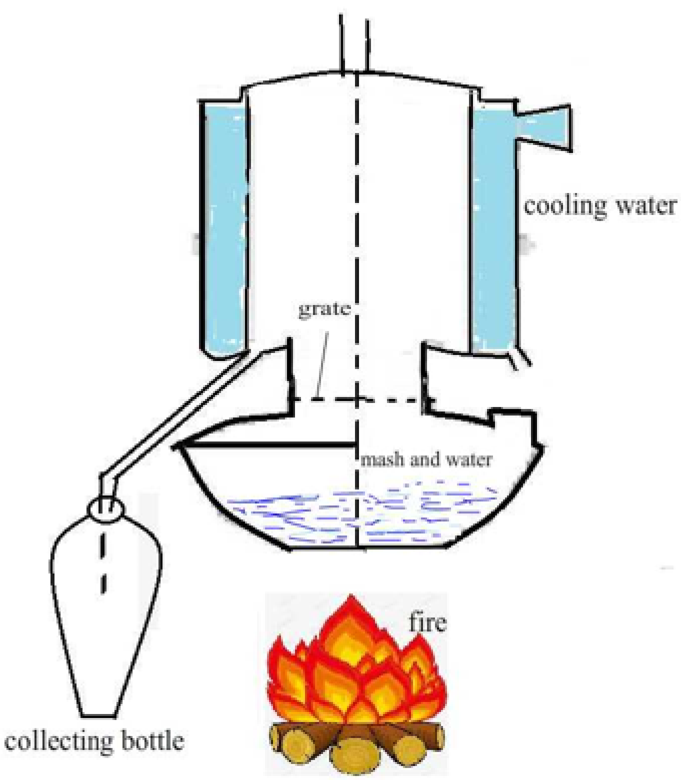

Figure 8

Steam distillation of B

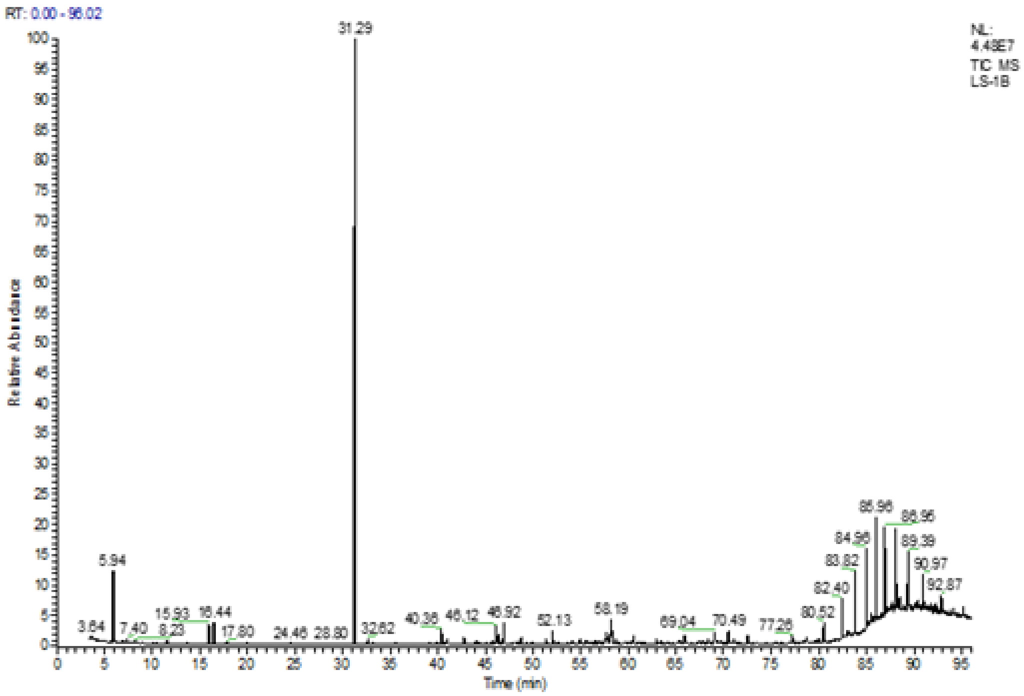

Figure 9

Total ion current chromatogram of volatile compounds in rose dew with A

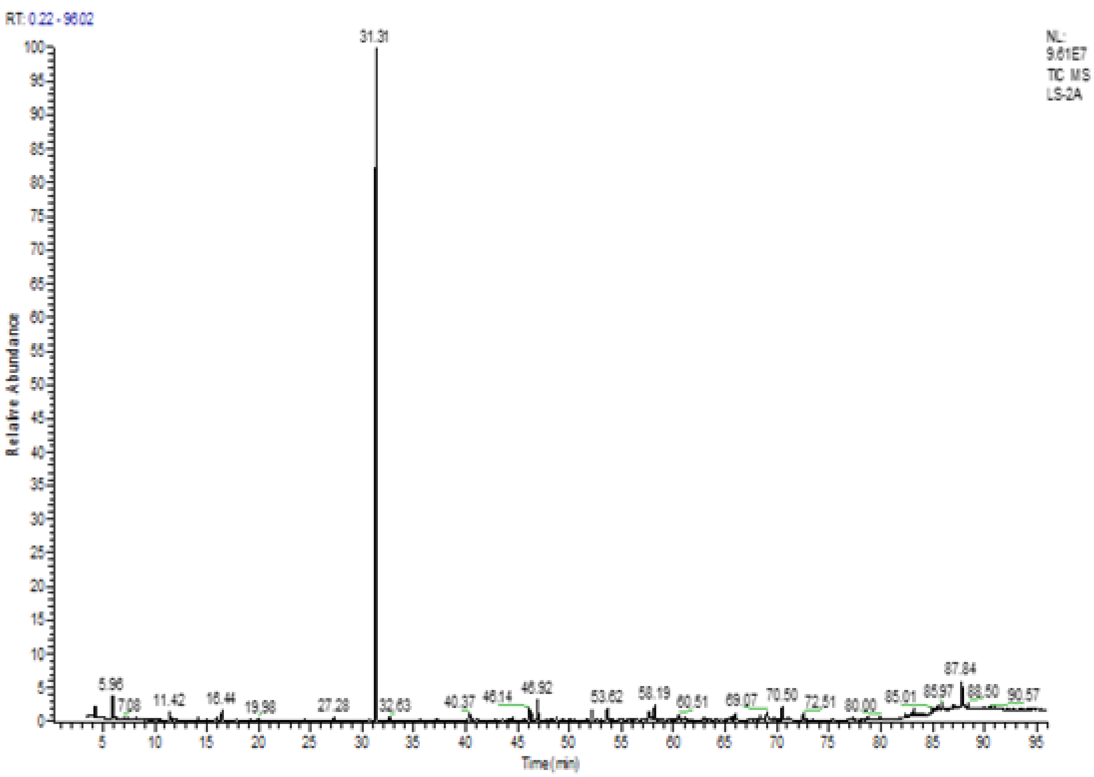

Figure 10

Total ion current chromatogram of volatile compounds in rose dew with B