Influence of the constituent alpha acids of Ukrainian varieties of hops and hop preparations on quality indicators of mash and beer

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Abstract

Introduction. The aim of the study is to establish the dependence of the bitterness of mash and the beer intoxication on the quality and quantity of the homologues of alpha acids in the Ukrainian varieties of hops, and on the content of cohumulone in alpha acids in particular.

Materials and methods. Aromatic and bitter hop sorts of Ukrainian selection with different content of cohumulone in alpha-acids were investigated and so was the beer, made of these components. High performance liquid chromatography (HPLC) was used to determine the amount and composition of bitter hop substances and their transformation products in the brewing process; also there were spectrophotometric methods for quality control of bitterness of hopped mash and finished beer in use.

Results and discussion. The composition of bitter substances of aromatic and bitter hop sorts of Ukrainian selection was analyzed and so the beer, made of them. It was noted that the alpha-acids of the analyzed sorts incorporate a wide range of cohumulone content rated from 16.7% in the Kumyr sort to 44,1% in the Ruslan sort. The dependences between the quality and quantity of the bitter hop sorts and bitterness and quality of hopped mash and beer were established. The content of cohumulone in alpha-acids of hops has to be less than 28% to obtain quality bitter beer. The role of the beta-acid compounds in the formation of bitter mash, hopped with aroma hop varieties with a ratio of beta to alpha acids acids around one, is much more important compared to the bitter varieties.

Conclusions. The conducted researches show that in applying the bitter hops with different compositon of alpha-acids for mash intoxication, this usage is more effective in the sorts that have a large content of cohumulone.

Introduction

Diverse in nature and chemical structure of substances that make up the hops give beer a typical bitter taste, specific aroma and determine many other important biotechnological properties. The compounds of hops are effective agents for the deposition of high-nitrogen compounds of mash take part in lighting , foaming, and exhibiting bactericidal and preserving effect on the final product, increasing the stability of beer in his storing.

In the previous studies of domestic and foreign scientists [1-4], it was found that beer brewed with hops or hop varieties of certain drugs varies considerably according to the nature of bitterness, flavor and aroma. This is due to the feature of the biochemical composition of bitter substances, polyphenolic compounds and essential oils of aromatic and bitter hop sorts. The different ratios of the components of these compounds influence the taste and aroma of beer in their own way. Therefore, the selection of sorts with optimal composition of bitter substances in order to brew beer with excellent quality and bitterness are the important issues as for the Brewers Association of America, so for European and Ukrainian brewers.

The major part in the formation of bitter beer [1,2,5] for hopping mash belongs to the alpha acids, which consist of humulone, cohumulone, adhumulone, prehumulone and posthumulone. Moreover, depending on the length of the side chains of acyl residue at the second carbon atom of the hexadiene ring changes the solubility of homologues of alpha acids; meanwhile, this rule takes place: the longer the side chain is, the lower is the solubility. That's why cohumulone's solubility is much higher, than humulone's or adhumulone's [1].

The isomers of original bitter hop substances, which are contained in its cones in small quantities and formed during boiling mash with hops, affect the specific qualities of beer the most. During boiling, alpha-acids transform into iso-alpha-acids and, as a result, the hexadiene ring of alpha-acids becomes a pentadiene ring of iso-alpha-acids [1]. The iso-alpha-acids are more soluble in mash and more bitter than alpha-acids [1, 2] and form 90 – 95% of the general bitterness of beer.

It is a known fact [1, 4], that isohumulone, isocohumulone and isoadhumulone have almost the same degree of bitterness. However, during boiling mash with hops isomerization of homologues of alpha – acids proceeds with the formation of various isocompounds. The proportion of homologues of alpha acids is very important here. Czech hops (sort Zhatetskyy) is characterized by high content of humulone , adhumulone (80%), while in German and American resinous sorts such as Hercules, Tomahawk cohumulone is predominant (50%). Cohumulone transfers into an isomer much better than the other alpha-acids' components, that's why the hop sorts with a high amount of cohumulone are more bitter. But this fraction is credited with a negative role in the formation of bitter beer [6]. However, although, humulone dominates in the Czech sorts composed of alpha acids, the bitterness if Czech beer is represented mainly by isohumulone. During the processing of hop varieties with superior content of cohumulone beer contains mostly iso-cohumulone , and the quality of bitterness, according to M. Kusche etc. is much worse [7, 8]. It is possible that the quality difference of the original alpha acids is at the same time the cause of a known difference in the quality of the bitterness of beer, which can be very essential. That is why the selection of varieties with optimal composition of bitter substances to obtain a beer of excellent qualified bitterness is a live issue to the Brewers Association of America [6] European brewers [7] and Ukrainian beer brewers [1].

As can be seen from the analysis of the literature, the composition of bitter hop substances of foreign sorts and their homologues' impact on the quality of bitter beer are

well studied. In contrast, similar studies with native hop varieties were barely held. In this regard, to ensure a stable and high-quality beer bitterness it is important to investigate the effect of individual components of the alpha acids of domestic varieties of hops and hop preparations on quality indicators of mash and beer.

The aim of the study was to establish the dependence of the bitter mash and the quality of beer intoxication on the quantity and the quality of the homologues of alpha acids of domestic hop sorts including the content of cohumulone composed of alpha acids.

Materials and methods

The researches were held in a certified laboratory of the department of Biochemistry of hop and beer Institute of Agriculture in Polessye of NAAS of Ukraine. The cones of aromatic and bitter hop sorts of Ukrainian selection of different content of cohumulone composed of alpha acids and beer made of them were investigated.

In the studies there were the modern international physical and chemical methods of analysis of bitter substances of hops and hop preparations and products of their transformation during brewing in use, such as: HPLC, spectrophotometry and also quality control methods of hopped mash of finished beer which are harmonized with the methods of the European Brewing Convention [1,9,10].

Methods of research of quality hop indicators. Sampling hops of each sort was carried out in the phase of full technical maturity. The average weight of a sample for identification and biochemical studies was at least 0.5 kg of dry hops.

The bitter hop substances are: α- and β – acids and their components, cohumulone in particular was extracted from the hop cones by an organic solvent – methanol. The ratio between the weight of hop cones and extractant was 1:10. The number of α-and β-acids and content of cohumulone in composition of α-acids were determined by high performance liquid chromatography. Chromatography was carried out using a liquid chromatograph Ultimate 3000 with UV detector at 35 degrees Celcium. The column with a size of 100 x 2.1 mm, which was filled with sorbent Pinacle DV C18 on 3 microns was used. The solution of methanol, water and acetonitrile was used as a mobile phase in the ratio of 38:24:38. The international standard ISF-3 was used for the quantitative determination of the components of bitter substances.

Methods of research of quality indicators of mash and beer. Experimental beer brewing with hop samples were conducted in the laboratory and in the Brewery Institute, with capacity of 100 liters of beer per cycle, which quite adequately simulates the real conditions of the brewing industry. The experimental preparation and congestion filtration were performed using an acceptable technology. Mash was prepared from 100% barley malt. After a full set mash was boiled for 30 min. Afterwards different hop sorts were put into mash in each option of the experiment; this process was represented in two installments: 85% at the beginning of intoxication, 15% - for 15 minutes. before the end of intoxication. The total duration of boiling mash with hops was 90 min. The bitterness of mash, which is formed in the process of boiling with hops as a result of extraction and isomerization of bitter hop substances, was determined on a spectrophotometer according to the method of EMU 8.8. (international method MI). The method is based on measuring the optical density of isooctane extract obtained by extraction of bitter hop substances of acidified hopped beer mash with isooctane (2,2,4-trimethylpentane) on a spectrophotometer at the wavelength of 275 nm against isooctane.The bitterness was calculated in terms of optical density; the quantity of bitterness is expressed in international units of bitterness - EMU units.

Results and discussion

The influence of cohumulone of bitter hop sorts on the quality of mash.

The bitter substances of hop sorts of Ukrainian selection, including alpha – acids, have a wide range of cohumulone content, rated from 16.7% in sort Kumyr to 44.1% in sort Ruslan. For research, we have selected hop varieties of bitter type with minor deviation of alpha acids and the ratio of beta acids to alpha-acids and with different content of cohumulone as a part of of alpha acids (Table 1).

Table 1

Characteristics of bitter substances of the studied hop varieties

№	Hop sort	Content of α - acids, %	Cohumulone in α - acids, %	Content of β - acids, %
1	Kumyr	7,2	16,7	3,9
2	Granite	7,2	19,6	3,3
3	Nasar	7,3	26,4	4,9
4	Promin’	7,5	29,0	4,1
5	Xanthi	6,2	35,1	4,0
6	Ruslan	6,7	44,1	4,7

The laboratory beer brewing was conducted with the given hop sorts, the number of alpha – acids and cohumulone, which was put in 1 dm^3 of mash, was calculated. The bitterness oh hopped mash was identified using spectrophotometer.

With the normalization of domestic hop varieties of bitter type, according to Industrial Technological Instructions, the same amount of alpha acids is put into mash (nearly 60 mg/dm^3) but a different amount of cohumulone rated from 10,0 mg/dm^3 in hop sort Kumyr to 26.4 mg/dm^3 in sort Ruslan. Thus, the magnitude of bitterness of hopped mash also varies from 33.1 units. EMU (sort Kumyr) to 41.1 units. EMU using hop varieties Xanthi, as reflected in fig. 1.

From the analysis of Table. 1 we see that in hops of sort Xanthi the amount of cohumulone composed of alpha acids was 52.2% more compared to the lowest content of cohumulone in hops of sort Kumyr. Thus, according to the data in Fig. 1 the quantity of bitterness of hopped mash increased by 19.5% compared to the sort Kumyr . That is, with increasing mass fraction of cohumulone composed of alpha acids of hop sort Xanthi by 1%, the value of of bitterness of hopped mash increases by 0.37%. During intoxication of mash by hop sort Ruslan with significantly higher content of cohumulone composed of alpha acid the quantity of mash virtually unchanges.But, if in hop sort Ruslan the amount of cohumulone composed of alpha acids was 62.1% more compared to the hop sort Kumyr, the value of bitterness of mash, hopped by this hop sort would increase only by 17.3% compared to the sort Kumyr. With the increase of mass fraction of cohumulone composed of alpha acids of sort Ruslan by 1% the quantity of of bitterness of hopped mash increases by only 0.28%. After analyzing the ratio between growth of cohumulone composed of alpha acids and the change of the value of bitterness of mash, hopped by the given hop sorts, the conclusion follows: with growing proportion of of cohumulone composed of alpha acids by 1%, the value of of bitterness of mash, hopped by the bitter domestic hop crops, increases from 0.24% for sort Granite to 0.42% for sort Promin’. The research findings expain why we do not always get a stable normalized beer bitterness during the normalization of mash on the content of alpha acids.

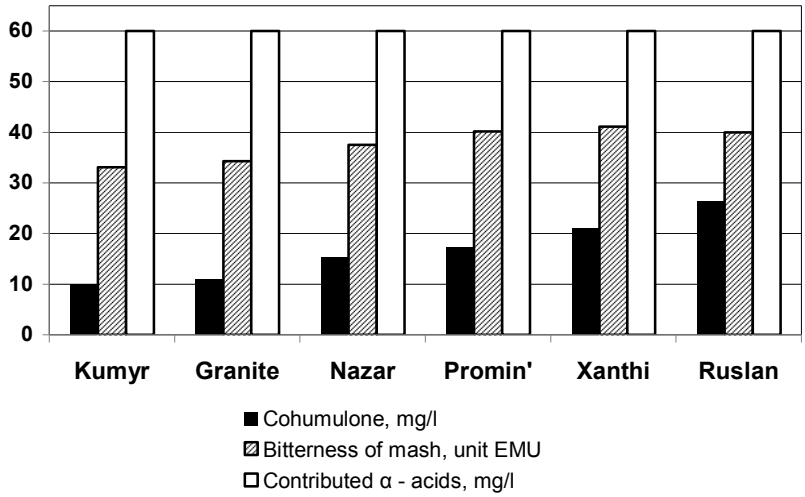

Fig. 1. The number of bitter hop substances, made to the mash and defined in it

It was found by the conducted studies, that at application for intoxication of mash by bitter hop sorts with different composition of alpha acids, it is more effective to use them for sorts with a high content of cohumulone.

The influence of cohumulone in aromatic hop sorts on the quality of mash and beer.

To establish the correlation dependencies, we have also chosen to study a group of aromatic hop varieties with different content of cohumulone composed of alpha acids and small deviation of ratio of beta – acids to alpha – acids (Table 2).

Table 2

The characteristic of bitter substances in aromatic hop varieties

№	Hop sort	Content of α - acids, %	Cohumulone in α - acids, %	Content of β - acids, %	Ratio of α/β – acids
1	Hmeleslav	3,7	22,1	4,1	1,01
2	Slavonian	4,6	23,3	5,9	1,29
3	Zagrava	6,1	25,6	6,6	1,06
4	Haidamak	4,8	28,8	5,6	1,17

At the mini – brewery of the Institute beer was brewed with the given hop sorts after laboratory beer brews and their analysis. The intoxication was performed by classical technology at the rate of 60 mg of bitter hop substances per 1 dm^3 of mash.

During the research we determined the number of put beta acids and cohumulone to 1 dm^3 of mash and the resulting value of mash, that is displayed in Figure 2.

The findings indicate that by the industrial technological Instruction, in normalization of various hop sorts the same amount of alpha acids is put into mash (60 mg/dm^3) but a different number of cohumulone (from 13.2 dm^3 in hop sort Hmeleslav to 17.3 dm^3 in sort

Haidamak. Herewith, The magnitude of bitterness of hopped mash also varies from 24.1 units EMU to 32.6 units EMU. But, if in a hop sort Haidamak the amount of cohumulone composed of alpha acids was 23.3% more compared to the lowest content of cohumulone in hop sort Hmeleslav, the value of bitterness of mash, hopped with a given hop sort, would increase by 26,1 % compared to Hmeleslav. So, with the increase of mass fraction of cohumulone composed of alpha acids of sort Haidamak by 1%, the quantity of of bitterness of hopped mash is increased by 1.1%, while for bitter hop sorts, which have a ratio of beta acids to alpha acids – 0,3-0, 6, this index was much lower and was only 0,24-0,42.

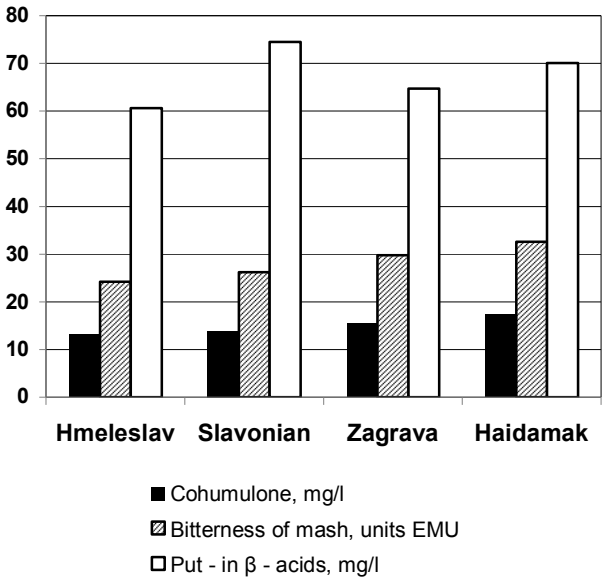

Fig. 2. The number of put – in and defined bitter substances of aromatic hop sorts in mash

The results revealed that in the formation of bitterness of mash, hopped with aromatic hop sorts from the ratio of beta acids to alpha acids around 1, the role of beta-acids' compounds is much higher compared to the bitter varieties.

The defined dependences are also stored in the study of finished beer, characteristics of which are shown in Table 3.

Table 3

The content of bitter substances and polyphenolic compounds in beer samples

№ sample	Hop sort of the beer	Bitterness of beer, units EMU	Total polyphenols, mg/dm^3
1	Hmeleslav	15,07	196,0
2	Slavonian	19,64	180,4
3	Zagrava	23,58	172,0
4	Haidamak	24,51	178,0

Organoleptic evaluation of beer was estimated on a closed tasting according to the requirements imposed on the given variety of beer in 25-point system (Instructions for technochemical control of the brewing industry from 25.12.90). Organoleptic evaluation of

the quality of beer prototypes and it's biochemical evaluation show that all the samples satisfied the requirements of current ISO 3888-99. Beer. General specifications, but but they differed greatly in taste, aroma and character of bitterness (Table 4).

Table 4

Technological evaluation of the studied hop varieties

Options	Names of quality indicators							
					Taste			
	Transparency	Colour	Foaming	Flavour	Fullness	Hop bitterness	Total evaluation in points	Evaluation
Hmeleslav	3	3	5	3,4	4,0	4,0	22,4	excellent
Slavonian	3	3	5	3,8	4,2	4,5	23,5	excellent
Zagrava	3	3	5	3,6	3,9	4,1	22,6	excellent
Haidamak	3	3	5	3,5	3,7	3,8	22,0	excellent

The conducted studies have shown that the best beer was received while hopping mash by a hop sort Slavonian with delicate aroma. Beer had a nice flavor, fresh hop aroma and delicate, unresidual bitterness. For the given beer sample with hop the smallest amount of cohumulone but the largest amount of beta – acids was put in (Fig. 2).

Beer with aromatic hop sorts of Zagrava and Hmeleslav also was of an excellent quality. Beer of these options had nice flavor and aromatic properties. The bitterness of the 1st sample was soft, bound, conformed with the composition of the drink, but insufficient. The third sample of beer had a balanced, intense, a little excessive, but pleasant bitterness.

The fourth sample of beer had a good taste, but it was inferior to the aroma and hop bitterness to other samples. The committee members noted the slightly rough bitterness.

We have noted that in the first sample of beer, which was made with a hop sort Hmeleslav with the smallest amount of cohumulone and beta acids, bitterness of beer was the lowest. With increasing content of cohumulone composed of alpha acids from 22.1% in hop sort Hmeleslav to 28,8% in sort Haidamak and with increasing amount of put – in cohumulone with the given hop sorts from 13.2 to 17.3 mg to 1 dm^3 the bitterness of beer also increases, as spectrophotometric so organoleptic. Thus, the content of cohumulone composed of alpha acids of hops should be less than 28% to obtain high-quality beer bitterness.

So, the different representatives of bitter hop substances have different bitterness both in total intensity and for individual taste nuances. Taking into account the maximum qualities of all the components of a group of bitter substances allows efficient use of the most expensive raw materials, creating new beers.

Conclusions

1. The quality and the quantity of of beer bitterness depends on the varietal characteristics of hops, that is, on the quantity and quality of the homologues of alpha-and beta-acids fraction.

2. When applying hops with a slight deviation of ratio of beta – acids to alpha – acids and different composition of alpha acids, for mash intoxication, more efficient use of it is for varieties with a high content of cohumulone. The content of cohumulone composed of alpha acids of hops should be less than 28% to obtain high-quality beer bitterness.
3. The role of the beta-acid compounds in the formation of bitter mash, hopped with aroma hop varieties with a ratio of beta to alpha acids acids around one, is much more important compared to the bitter varieties.

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