

Super carbon dioxide extracts of spices. 3. Hop (*Humulus lupulus* L.)

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Summary

The composition of the hop extract obtained by extraction with liquid CO₂ under different conditions has been investigated. The highest yield of extract (9.7%) is obtained at temperature of 18-22°C, pressure of 54-58 atm. and time of 210 min. The extract contains 44.6% of α - and 19.3% of β -acids and it can be used in brewing.

Key words: hop extract, α - and β -acids

Hop (*Humulus lupulus* L.) is a perennial dioecious plant of the hemp family (*Cannabaceae*). Raw material are the cones, which contain 0.5%–1% of essential oil, 12%–21% of bitter substances, 2.5%–6.0% of tannins, cellulose, protein substances, lipids, waxes etc. [1]. Most valuable for brewing, where hop is mainly used, are the bitter substances, followed by the essential oil and tannins. The chief representative of α -acids is humulone, while those of β -acids – lupulone, adlupulone and colupulone, which add the bitterness to hop products [2, 3].

Hop processing with CO₂ is not a novelty and the extracts that are obtained are used mainly in brewing and in cosmetic industry. Depending on applied technological parameters the extracts that are obtained have different indexes [4-8]. Langezaal et al. [4] extract hop at pressure of 12.6-20.2 MPa and temperature of 40-60°C. Verschuere et al. [5] conduct the process at pressure of 25.3 MPa and temperature of 50°C, obtaining an extract with high content of essential oil, which is rich in myrcene, caryophyllene and humulene. Arandjietovic et al. [6] establish that the optimal conditions for extraction are temperature of 30°C, pressure of 250 bar and duration of 5 h. The content of α - and β -acids in the extracts that are obtained from them depends on the hop variety and is 16-34% and 30-53%, respectively. Buckee [7], comparing different hop products used in brewing, estab-

lishes the highest content of α -, iso- α - and β -acids in CO₂ extract. Similar results were obtained by Kotarska-Markowicz and Góra [8], who analysed water-alcohol and CO₂ extracts of hop for application in cosmetics. According to them, the CO₂ extract contains more essential oil and bitter substances.

In Bulgaria hop is processed only by extraction with methyl alcohol, because of which the aim of the present work is to investigate the opportunity for obtaining extract with CO₂, with high content of bitter acids and the possibility to be applied in brewing.

EXPERIMENTAL

Plant material

Hop in granules was used, variety Nuhett, given by the firm Bulhops–Velingrad, Bulgaria, with the following indexes: moisture of 9.3% (determined by azeotropic distillation), the contents of α - and β -acids of 9.2% and 3.1%, respectively (recalculated against absolute dry substance).

Isolation of the extracts

The air-dried granules of hop were extracted with liquid CO₂ in a laboratory extractor under different conditions, as shown in Table 1.

Table 1.

Extraction conditions.

No	conditions			
	temperature, °C	pressure, atm.	time, min	extraction method
1	22-26	60-66	90	static with twofold overflow
2	22-26	60-66	90	continuous flow
3	up to 38	78-82	90	super critical conditions
4	38-42	78-82	90	super critical conditions
5	18-22	54-58	90	continuous flow with
6	18-22	54-58	270	draining every 30 min

Identification of components

The content of α - and β -acids is determined by the methods of the European Brewing Convention [9], which consists in spectrophotometering at λ 275, 325 and 355 nm of methanol solutions obtained from the raw material and the ex-

tracts obtained from it, which are preliminary treated with toluol. The calculations are made by the formula of Alderton:

$$\alpha\text{-acids} = 0.667[73.79.D_{325} - 51.56.D_{355} - 19.07.D_{275}],$$

$$\beta\text{-acids} = 0.667[55.57.D_{355} - 47.59.D_{325} + 5.1.D_{275}],$$

where D is optical density, at corresponding wave length.

DISCUSSION

The analyses of the extracts and the residual raw materials are shown in Table 2. The data show that the highest yield which approximates the yields in the literature [3, 7] is obtained in the case of variant 6. In this case the bitter acids are extracted to the fullest from the hop, and in the residual raw material remain at the levels of 24% and 27%, respectively, of their content in the initial raw material. The extract contains above 30% of α -acids, which is an indication of high quality [3, 7, 8]. In the case of variants 2 and 3 the quantity of bitter acids is higher in comparison with variant 6, but the yield of extract is 2%–2.5% lower. For variants 1, 2 and 4 the content of bitter acids in the residual raw material is not determined because of the low yield of the extract obtained.

Table 2.

Indexes of the extracts and the residual raw material.

No	extracts			residual raw material	
	yield, %	α -acids, %	β -acids, %	α -acids, %	β -acids, %
1	1.2	25.9	18.2	-	-
2	3.7	40.2	20.8	-	-
3	4.1	43.8	23.5	8.1	1.3
4	1.8	14.9	15.4	-	-
5	6.3	29.6	8.3	4.6	1.0
6	9.7	36.1	19.5	2.2	0.8

- not determined

In the case of variants 5 and 6 an extract is drained every 30 minutes, which is then analysed for the content of α - and β -acids. The data are shown in Table 3. As for variant 5, after 30 minutes the content of bitter acids reduces. As for variant 6, from 90 to 210 minutes an increase in the quantity of α -acids is observed, from 32.1% to 44.6%, while the content of β -acids decreases.

Table 3.

Indexes of the extracts of variants 5 and 6.

time, min	variant 5		variant 6	
	α -acids,%	β -acids,%	α -acids,%	β -acids,%
30	31.7	23.3	22.3	20.1
60	29.2	22.9	27.7	20.1
90	26.0	18.7	32.1	20.8
120	-	-	35.9	18.5
150	-	-	40.5	18.8
180	-	-	44.9	18.8
210	-	-	44.6	19.3
240	-	-	43.3	16.9
270	-	-	39.3	14.5

- not determined

In conclusion, for extraction of hop with CO₂ under the following conditions of experiments: temperature of 18-22°C, pressure of 54-58 atm. and time of 210 min, an extract with high content of bitter acids is obtained, which conforms to the extract in the existing standards, as far as indexes are concerned.

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EKSTRAKTY WYSOKOCIŚNIENIOWE UZYSKANE Z ROŚLIN PRZYPRAWOWYCH
ZA POMOCĄ CO₂. 3. CHMIEL (*HUMULUS LUPULUS* L.)

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Streszczenie

Badano skład ekstraktu uzyskanego z chmielu za pomocą ciekłego dwutlenku węgla w różnych warunkach doświadczalnych. Największą ilość ekstraktu (9,7%) uzyskano przy temperaturze 18-22°C i ciśnieniu 54-58 atm utrzymanych przez 210 minut. Ekstrakt zawiera 44,6% α-kwasów oraz 19,3% β-kwasów i może być wykorzystywany w piwowarstwie.

Słowa kluczowe: ekstrakt chmielu, α-kwasy i β-kwasy