Changes of Hop Prenylflavonoids Content During Maturation, Harvesting, and Processing

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Abstract

Changes to the content of the hop prenylflavonoids were tested in the Czech variety Vital during three vegetation seasons. While xanthohumol is a very stable compound, desmethylxanthohumol (DMX) is prone to decomposing under heat exposure and open air conditions. Monitoring of DMX in green cones during ripening and maturation showed that the content of DMX in green cones reached the level of 0.50-0.70% w/w in dry matter. A dramatic decrease in the DMX content by more than 50% rel. occurred during the full scale drying in belt dryers. The content of desmethylxanthohumol showed a permanently decreasing trend depending on the processing and storage conditions. The total loss of DMX in the chain of mature green cones-dry cones-pellets-CO_2-extraction/spent hops reached up to 65-75 % rel. In spite of this, the residual content of DMX in spent hops was mostly found in the range of 0.15-0.20 % w/w. The CO_2-extraction seems to be the most convenient processing method with respect to the prospective utilizations of spent hops which contain high amount of prenylflavonoids. The experiments resulted in a proposition of several measures in order to preserve the prenylflavonoids contents in hops at the highest possible level.

Key words: hops, Vital variety, hops processing, xanthohumol, DMX

Introduction

The xanthohumol and desmethylxanthohumol (DMX) prenylflavonoids are important secondary metabolites in hops. Numerous studies have proven a considerable number of beneficial physiological and medical effects of xanthohumol (Gernhauser, 2002; Stevens, 2004; Lupinacci, 2009). DMX is a potential precursor of 8-prenylnaringenin, which is the most potent known phytoestrogen (Fig. 1) (Milligan, 2002). Changes to the content of the above mentioned prenylflavonoids were tested in the Czech variety Vital in the chain mature green cones-dry cones-pellets-CO_2-extraction/spent hops during three vegetation seasons 2010–2012. The Vital variety has an above the average content of xanthohumol (0.70-0.90% w.) and a high content of DMX (0.20-0.40% w.) in dried cones immediately after harvesting (Krofta, 2013). These characteristic properties may be utilized in other industry branches like the pharmacy or the food supplements production.

Material and Methods

Content of prenylflavonoids was monitored during hop cones maturation till harvest in samples of green cones taken on hop gardens in three vegetation seasons 2010-2012. Drying process was analytically followed in pilot scale chamber dryer and results compared with drying in full scale belt dryer during mechanized harvesting. Analytical control of hop pellets, CO_2-extracts a spent hops after extraction was done too. Contents of prenylflavonoids xanthohumol and DMX as well as of alpha and beta acids in hops samples were measured by modified EBC 7.7 method. Analytical signal was monitored at the wavelenghts of 314 nm (alpha, beta acids) and 370 nm (xanthohumol, DMX). Green hop cones were cut to small pieces before extraction. Moisture content in green hops were determined according to EBC 7.2 method.

Results and Disscussion

Hop plants of Vital variety are able biosynthetize high amount of both prenylflavonoids, 0.70-.0.90 % w/w of xanthohumol and 0.50-0.70 % of DMX in a dry matter (Table 1). During full scale drying at the temperature of 55 °C is appr. half of original amount of DMX decomposed. Drying in pilot-scale chamber dryer at the temperature of 45 °C provided much better results (Table 2). The content of desmethylxanthohumol showed a permanently decreasing trend during further processing to pellets or CO_2-extract depending on the processing and storage conditions (Table 3). It is necessary to store the harvested hops immediately after packaging in an air-conditioned warehouse. The total loss of DMX in the chain of mature green cones-dry cones-CO_2-extraction-spent hops reached up to 70% rel. (Fig. 2). In spite of this, the residual content of DMX in spent hops was mostly found in the range of 0.15-20% w/w. On the contrary, the losses of xanthohumol were very minor (Fig. 3). The CO_2-extraction seems to be the most convenient processing method with respect to the prospective utilizations of spent hops which contain the relatively hight amount of prenylflavonoids.

The experiments resulted in a proposition of several measures in order to preserve the prenylflavonoids contents in Vital hops at the highest possible level.

- *monitoring of prenylflavonoids content in green cones during maturation till harvest*
- *to start harvesting after full ripeness of hop achievement*
- *preference chamber dryers over belt ones*
- *maximum hops temperature during full scale kilning should not exceed temperature 50 °C*
- *storage of dry hops in air-conditioned warehouse at max. temperature +5 °C*
- *arrangement of logistic conditions during subsequent processing to pellets or extracts so that minimize exposition of hops to high temperatures*
- *pellets or spent hops after CO_2-extraction place into air-conditioned warehouse as quick as possible*
- *delivery of spent hops, usually packed in big volume wrapping pockets, to final customer in a short time*

Conclusion

Desmethylxanthohumol, on the contrary of xanthohumol, is thermally labile hop component. Its losses during drying and processing to pellets or extracts are inevitable. Process conditions and logistic operations should to be adjusted so that losses of DMX were as low as possible.

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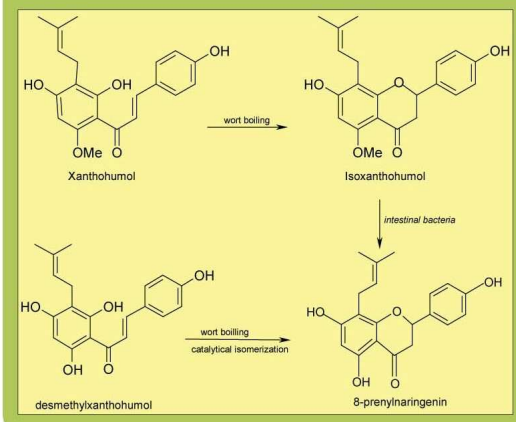
Fig. 1: Structures of xanthohumol, isoxanthohumol, DMX and 8-prenylnaringenin



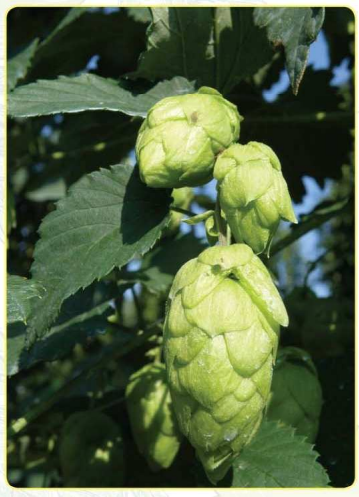


Table 1: Contents of alpha acids, beta acids and prenylflavonoids in Vital variety during hop maturation in season 2012 (experimental farm of HRI in Steknik)

Date of sampling	Alpha acid* (% w/w)	Beta acid* (% w/w)	Cohumulone (% rel.)	Xanthohumol* (% w/w)	DMX* (% w/w)	Moisture (% w/w
14. September	10,92**	11,17	19,9	0,78	0,51	75,6
	11,18***	11,15	20,2	0,81	0,52	
20. September	13,69	9,83	20,0	0,80	0,45	75,0
	13,36	8,98	19,6	0,71	0,39	
27. September	13,67	8,57	17,7	0,77	0,49	75,5
	13,35	7,96	18,1	0,75	0,46	
3. September	13,90	8,93	20,0	0,70	0,51	75,7
	13,29	9,46	19,7	0,68	0,51	
7. September	15,24	9,96	20,7	0,72	0,61	75,2
	14,24	10,20	20,9	0,74	0,60	

*contents are based on dry matter
**duplicate analyses

Table 2: Drying test of Vital variety in a pilot-scale chamber dryer at the temperature of 45 °C

Drying time (hours)	Alpha acids* (% w/w)	Beta acids* (% w/w	Xanthohumol* (% w/w	DMX * (% w/w)	Moisture (% w/w
green hops	12,74	8,25	0,82	0,45	74,0
	12,93	8,12	0,82	0,47	74,8
2 hours	13,03	8,50	0,83	0,41	52,5
	13,18	8,36	0,79	0,40	
4 hours	13,19	8,16	0,86	0,39	38,3
	13,34	7,90	0,83	0,38	
6 hours	13,16	8,38	0,90	0,38	30,0
	13,66	8,70	0,92	0,42	
8 hoursr	12,99	7,87	0,78	0,37	21,4
	12,79	8,48	0,85	0,38	
10 hours	13,19	8,48	0,87	0,38	16,7
	13,00	7,81	0,89	0,40	

*contents are based on dry matter

Table 3: Contents of alpha acids, beta acids and prenylflavonoids in Vital variety during full scale drying, pelletizing and CO_2-extraction (seasons 2010-2012)

Year of harvest	Hop product	Alpha acids* (% w/w)	Beta acids* (% w/w)	Xanthohumol* (% w/w)	DMX* (% w/w)
2010	dry hops**	14,7	9,1	0,78	0,36
	pellets T90	13,8	8,4	0,75	0,26
	CO_2-extract	47,0	28,2	-	-
	spent hops	1,08	0,58	0,83	0,21
2011	dry hops**	12,6	8,5	0,86	0,28
	pellets T90	9,3	6,1	0,66	0,16
	CO_2-extract	36,9	23,5	-	-
	spent hops	1,00	0,39	0,65	0,11
2012	dry hops**	13,7	8,4	0,74	0,31
	pellets T90	-	-	-	-
	CO_2-extract	42,9	26,5	-	-
	spent hops	0,24***	0,17***	0,87***	0,18***

*contents are based on dry matter
**full scale belt dryer, drying temperature 55 °C
***another extraction processing facilities

Fig. 2: Contents of DMX in Vital hop variety in the chain green hops - CO_2-extraction spent in crop harvests 2010-2012

Year	Green cones	Dry hops	Pellets T90	Extraction (spent)
2010	0,63	0,36	0,26	0,21
2011	0,46	0,28	0,16	0,11
2012	0,60	0,31	-	0,18

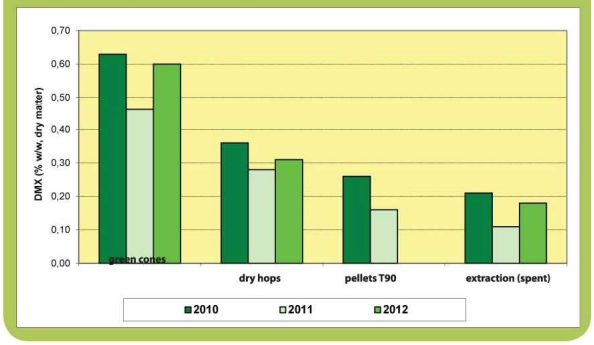


Fig. 3: Contents of xanthohumol in Vital hop variety in the chain green hops - CO_2-extraction spent in crop harvests 2010-2012

Year	Green cones	Dry hops	Pellets T90	Extraction (spent)
2010	0,78	0,78	0,75	0,83
2011	0,82	0,86	0,66	0,65
2012	0,75	0,74	-	0,87