

# Hop Bioactive Compounds: Spontaneous vs Commercial Varieties

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## Introduction

*Humulus lupulus* L. is a species belonging to the Cannabaceae family. Hop, as it is commonly known, is a perennial, dioecious and normally diploid ( $2n = 20$ ) herbaceous plant. It is in beer production that hops have their greatest economic value at the international level. In addition, Hop contains compounds that confer sedative, diuretic anti-inflammatory and antiarthritic properties [1]. In fact, the ethnobotanical uses of the dried flowers in pillows called "hop pads" have been used to combat insomnia while the dried and green hop inflorescences, were used in the Montesinho park area to treat urinary and digestive disorders [2]. Since there are spontaneous hops in a large part of Portugal, the collection and analysis of the volatile,  $\alpha$  and  $\beta$ -acids component, and phenols of these hops may lead to the development of new and more fragrances, and bioactive compounds with interest in different areas, like beer production or pharmaceuticals and cosmetics. The analysis of these compounds was done in commercial and spontaneous varieties collected in the Bragança area (northeast of Portugal).

## Material and Methods

Spontaneous hop samples were collected from different areas of Bragança district and were analyzed and compared with commercial varieties (Nugget, Polaris, Cascade and Chinook). Being the volatiles extracted from the female cones, leaves and pellets (used in brewing) using a Likens-Nickerson system, and analyzed by GC and GC-MS. The  $\alpha$  and  $\beta$  acids, from varieties and spontaneous, were extracted and analyzed by HPLC. We extracted the phenolic compounds using a mixture of 80% ethanol and 20% water. The hop varieties used for the extraction were, for the vegetative parts: Chinook, Cascade, Polaris, Centennial, Nugget, and spontaneous plant and for the flowers: Cascade, Polaris, Nugget, Centennial, and the spontaneous. We used The Folin-Ciocalteu method was used to determined the amount of phenolic compounds [3].

**Table 2:** Volatiles from vegetative part flower and pellets of the spontaneous and varieties

Compounds	RI	PELLETS										FLOWERS									
		Casca-de-2017	Casca-de-14-2017	Chinook-2017	Nugget-3-2017	Nugget-3-2017	Polaris-2-2017	Chinook-4-2017	Polaris-5-2017	Al-Falco-6-2017	France-14-2017	Casca-de-pellets	Centennial-C1-pellets	Chinook-C2-pellets	Casca-de-13-folhas	Casca-de-folhas	Centennial-folhas	Chinook-folhas	Nugget-14-folhas	Nugget-folhas	
Isomyl alcohol	636																				
Isomyl acetate	908																				
$\alpha$ -Pinene	930	0.2			0.2	3.0	0.1	0.6	0.3	0.1	0.2	0.3	0.2	0.6	0.1	0.9	0.6			0.1	
Hexanoic acid	968																				
Ethyl hexanoate	975																				
$\beta$ -Bisabolene	978	73.9	61.4	36.0	74.9	12.0	49.7	1.0	33.6	33.6	64.4	64.9	74.4	47.6	2.2	2.6	4.6	5.5	1.1	3.1	
Limonene	1009	0.2	0.3	0.2	0.9	1.8	2.0	3.8	9.3	5.0	0.2	0.8	0.6	9.3	14.2	12.4	20.3	20.5	7.5	14.0	
n-Octanol	1045																				
Fenchone	1050																4.1	6.7	7.7	0.4	4.4
Phenylethyl alcohol	1064																				
Linalool	1074	0.3	1.2	0.2	0.3	1.3	1.0	1.6	1.7	1.1	0.7	0.7	1.0	0.5			2.7	5.0	4.4	0.2	3.0
Camphor	1102																				
Borneol	1134																				
Terpinenol	1148																				
Oxenoic acid	1152																				
Ethyl octanoate	1177																				
Phenylethyl acetate	1229																				
Pulegone	1207																				
Linyl acetate	1245																				
2-Undecanone	1275	0.3			0.2	1.0	0.3	3.6													
Carvone	1296																				
Methyl geranate	1298																				
Decanoic acid	1350																				
Ethyl decanoate	1397																				
$\beta$ -Caryophyllene	1414	4.0	6.2	9.6	9.5	3.0	3.9	0.7	2.2	4.5	1.5	4.8	4.0	7.2	13.4	16.5	6.9	6.9	14.5	8.7	
$\beta$ -Cedrene	1426	0.2			0.1																
n-Humulene	1447	8.5	14.6	19.7	12.1	12.6	7.7	0.7	0.4	0.8	0.2	12.1	7.7	14.4	13.9	16.5	3.9	9.0	22.8	12.4	
trans- $\beta$ -Farnesene	1455	3.7																			
$\gamma$ -Muurolene	1469	0.2	0.4	2.1	0.2	1.1	0.7	2.1													
Germacrene D	1474																				
Valencene	1474																				
Bicyclogermacrene	1497																				
$\gamma$ -Cadinene	1500	0.6	0.4	2.0	0.3	2.0	0.5														
$\beta$ -Cadinene	1505	0.5	0.6	3.3	0.5	1.2	0.5														
Germacrene B	1535																				
$\beta$ -Caryophyllene oxide	1561																				
Ethyl decanoate	1580																				
Humulone oxide	1580																				
$\beta$ -Eudesmol	1620																				
$\alpha$ -Eudesmol	1634																				
Monoterpene hydrocarbons	75.7	63.4	38.0	77.0	16.5	46.9	5.6	44.7	39.5	65.7	66.7	75.9	51.6	10.0	15.5	26.0	27.3	9.3	18.2		
Oxygen-containing Monoterpenes	0.7	1.2	0.2	0.3	3.3	1.8	5.0	14.7	3.5	0.7	2.1	4.7	1.7	11.5	16.8	34.4	28.9	1.3	19.9		
Sesquiterpene hydrocarbons	17.7	21.0	41.6	16.9	22.4	33.9	19.2	17.0	13.4	16.6	24.7	13.6	29.7	35.6	45.5	11.0	23.2	65.0	41.3		
Oxygen-containing Sesquiterpenes	0.0	0.4	0.9	0.1	0.0	1.2	7.6	2.0	3.7	2.4	0.9	0.1	0.9	5.4	8.5	8.3	4.5	3.4	5.6		
Others	0.3	1.7	0.2	0.8	1.7	1.5	4.9	0.6	0.9	3.5	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0		
	34.4	89.7	81.7	95.1	45.9	85.3	42.3	79.0	61.0	88.9	94.5	94.3	83.9	71.3	86.3	75.7	83.9	79.0	85.0		

RI - Retention index relative to n-alkanes C<sub>8</sub>-C<sub>17</sub>

Varieties  
Spontaneous

## Conclusion

The  $\alpha$  and  $\beta$  acid and volatiles we find in the spontaneous clone had values close to the Cascade variety which may be interesting in the development of new aroma varieties. The richness of the spontaneous clone in trans- $\beta$ -farnesene can be determinant to the stability of the beer, or used in cosmetic products. In the phenols the results are still preliminary, in general, flower extracts are richest in phenolic compounds with potential for further use in e.g. cosmetics.

## Results

The results show similarity in the monoterpene component, with  $\beta$ -myrcene as the major compound (more than 64% in all the samples) and differences in the sesquiterpene component, e.g. of  $\alpha$ -humulene (12% in cultivars, 0.2% in spontaneous) and trans- $\beta$ -farnesene (not detected in Nugget and 9% in spontaneous, Cascade variety was detected 3.7% in cones and 4.7% in pellets, in Polaris variety were 15%). The richness of the sesquiterpene component in spontaneous clone is notable, namely in the oxygenated compounds. The higher values, of the  $\alpha$  and  $\beta$ -acids component in the cultivar Nugget, is expected since is a bitter variety, due to its acids amount. The cultivars presented total values of 12.12% and 14.33% of  $\alpha$ -acids and 3.31% and 3.99% of  $\beta$ , respectively, while the spontaneous clone presented 5.35% of  $\alpha$ -acids and 4.3% of  $\beta$ . The results from phenols in flowers and vegetative parts, shown the flowers contained a large amounts of phenolic compounds than the same vegetative parts, with higher amounts in the spontaneous concerning the vegetative part and Polaris variety for the flowers. The composition of the extracts from vegetative parts and flowers of Cascade variety were mainly flavonols glycosides.

**Table 1:**  $\alpha$ ,  $\beta$  acid results in flower, vegetative parts and pellets of varieties and spontaneous

	$\alpha$ acids		Total	$\beta$ acids		Total
	Co-Humulone	n+ad Humulone		Co-lupulone	n+ad lupulone	
Wild clone	3,00%	4,30 %	7,30 %	4,30%	4,30%	8,60%
Nugget (flower)	2,40%	9,63%	12,20%	1,49%	1,82%	3,31%
Nugget (flower)	3,10%	11,23%	14,33%	1,86%	2,13%	3,99%
Cascade (flower)	1,451%	3,082%	4,533%	2,963%	2,671%	5,634%
Chicook (flower)	3,96%	10,447%	14,401%	2,570%	2,018%	4,588%
Cascade (pellets)	1,40%	2,69%	4,09%	3,33%	2,60%	5,93%
Chinook (pellets)	2,88%	6,37%	9,25%	1,75%	1,26%	3,01%
Centennial (pellets)	1,88%	5,19%	7,07%	1,71%	1,43%	3,14%

**Table 3:** Total phenol compounds express in Gallic acid 1-hydrate, in the diferente plants extracts

Sample	Total Phenolic Compounds (mg GAE/g dried plant)	
	Vegetative parts	Flowers
Cascade	2.05±0.66	10.39±2.05
Polaris	1.05±0.22	22.71±2.44
Centennial	1.65±0.38	9.68±1.61
Nugget	0.84±0.24	14.80±1.06
Chinook	1.75±0.50	-
Spontaneous	3.08±0.53	-

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