Hop Bioactive Compounds: Spontaneous vs Commercial Varieties

Hugo Goes[1,2], Luís Pedro[3],Olívia R. Pereira[1,2], Jorge Sá Morais,[1,2] Mª João Sousa[1,2, *]

1 Mountain Research Centre - Escola Superior Agrária-Instituto Politécnico de Bragança, Campus de Santa Apolónia, Apartado 117, 5301-855 Bragança, Portugal
2 Polytechnic Institute of Bragança - Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
3 Centro de Estudos do Ambiente e do Mar (CESAM), Faculdade de Ciências da Universidade de Lisboa, Centro de Biotecnologia Vegetal (CBV), C2, Piso 1, Campo Grande, 1749-016 Lisboa, Portugal

*joaos@ipb.pt

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, α and β-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 pharmaceutics 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 α and β 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-Ciocalteau method was used to determined the amount of phenolic compounds [3].

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

		CONES										PELLETS			FOLHAS					
Comprtes	RI	Cascade 2017	Cascade H1_2016	Chinook 2017	Nugget 2017	Nugget_3 (flores)	Polaris_2 (flores)	Oleiri-nhos_4 (flores)	Fervença_5 (flores)	Alfaião_6 (flores)	França (Amostra 3)	Cascade_pellets	Centenni-al_C1_pellets	Chino-ok_C2_pellets	Cascade_L3_folhas	Cascade_folhas	Centenni-al_folhas	Chino-ok_folhas	Nugget_L4_folhas	Nugget_folhas
Isoamyl alcohol	836																			
Isoamyl acetate	908																			
α-Pinene	930		0,2		0,2	3,0	0,1	0,6	0,3	0,1	0,2	0,3	0,2	0,2	0,6	0,1	0,9	0,6		0,1
Hexanoic acid	968																			
Ethyl hexanoate	975																			
β-Myrcene	975	73,9	61,4	38,0	74,8	12,0	43,7	1,0	33,6	33,6	64,4	64,9	74,4	47,5	2,2	2,6	4,6	5,5	1,1	3,1
Limoneno	1009	0,2	0,3	0,2	0,3	1,8	2,0	3,8	9,3	5,0	0,2	0,8	0,6	3,3	14,2	12,4	20,3	20,5	7,5	14,0
n-Octanol	1045																			
Fenchone	1050						0,3		2,5	0,7						4,1	5,7	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		3,0
Camphor	1102						0,1	1,3	7,1	0,2						1,4	2,1	2,2	0,2	1,3
Borneol	1134					0,3										0,2	0,4			0,2
Terpinen-4-ol	1148						0,1		0,6	0,3						1,0	2,2	1,5		1,1
Octanoic acid	1152																			
Ethyl octanoate	1177																			
Phenylethyl acetate	1228																			
Pulegone	1207						0,2		0,9	0,5						4,8	11,5	7,8		6,3
Linalyl acetate	1245							1,3		0,2						0,7	1,5	1,1	0,2	0,9
2-Undecanone	1275	0,3			0,2	1,0	0,3	3,6		0,7	2,2	0,2								
Carvacrol	1286								0,7	0,3					11,5	1,7	4,4	3,9	0,3	2,5
Methyl geranate	1288											0,2	2,4	0,5						
Decanoic acid	1350																			
Ethyl decanoate	1387																			
β-Caryophyllene	1414	4,0	6,2	9,6	3,5	3,0	3,9	0,7	2,2	4,5	1,5	4,8	4,0	7,2	13,4	16,5	6,3	5,9	14,5	8,7
β-Copaene	1426	0,2		0,9	0,1								0,1	0,4	0,6	0,7		0,7	2,6	1,8
α-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-β-Farnesene	1455	3,7					14,7				8,5	4,7				0,6		0,4		0,8
γ-Muurolene	1469	0,2	0,4	2,1	0,2	1,1	0,7	2,1			0,6	0,5	0,3	1,7	1,7	2,0		2,2	5,2	4,0
Germacrene D	1474															1,0			7,2	4,0
Valencene	1484						2,5				2,2									
Bicyclogermacrene	1487							6,4	8,7											
γ-Cadinene	1500	0,6	0,4	2,0	0,3	2,8	0,5				0,2	0,9	0,7	1,6	1,1	1,4		1,5	4,9	3,7
δ-Cadinene	1505	0,5	0,6	3,3	0,5	1,2	0,5		0,4			0,8	0,6	2,7	1,6	2,0	0,8	2,5	7,1	4,9
Germacrene B	1533			1,9			1,5		3,2	7,2	1,1									
β-Caryophyllene oxide	1561		0,2	0,3							0,2				4,4	3,8	4,4	1,6	1,0	1,9
Ethyl decanoate	1580																			
Humulene oxide	1580											0,3				3,8	3,9	2,9		2,7
β-Eudesmol	1620						0,4	3,2	0,5	1,2	0,6									
α-Eudesmol	1634						0,7	3,0		1,6	0,7									
Monoterpene hydrocarbons		75,7	63,4	38,8	77,0	18,5	46,9	5,6	44,7	39,5	65,7	66,7	75,9	51,6	18,8	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	23,0	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	65,8	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	0,3	0,1	0,9	5,4	8,5	8,3	4,5	3,4	5,6
Others		0,3	1,7	0,2	0,0	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
		94,4	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	79,7	83,9	79,8	85,0

RI - Retention index relative to n-alkanes C_8-C_{17}

Varieties
Spontaneous

Conclusion

The α and β 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-β-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 β-myrcene as the major compound (more than 64% in all the samples) and differences in the sesquiterpene component, e.g. of α-humulene (12% in cultivars, 0.2% in spontaneous) and trans-β-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 α and β-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 α-acids and 3.31% and 3.99% of β, respectively, while the spontaneous clone presented 5.35% of α-acids and 4.3% of β. 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: α, β acid results in flower, vegetative parts and pellets of varieties and spontaneous

	α acids		Total	β 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

	Total Phenolic Compounds (mg GAE/g dried plant)	
Sample	**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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