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Effect of Hop Varieties Aram is, Mistral and Barbe Rouge on Beer Aroma During Dry Hopping

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Effect of Hop Varieties Aram on Beer Aroma During Dry

BOUQUET ANALYSIS | In recent years, the dry hopping technique was developed to produce unique beers by revealing all the aromatic potential of hops. The aim of this study was to investigate the impact of hop varieties Aramis, Mistral and Barbe Rouge on the sensory properties of dry-hopped lagers. Analysis of volatile compounds and sensory ranking tests of beers revealed that these three hops have unique aromatic signatures.

DRY HOPPING was defined in the last decades as an uncommon technique used by craft brewers to enhance the aroma of their beers. This end of process technique allows to greatly improve the volatile compounds brought by hops in beer.

During the traditional beer process (late process), most of the volatile compounds brought by hops are lost by evaporation, chemicals and enzymatic transformations [1]. In dry-hopped beers most of the hop volatile compounds are preserved. Among these compounds, terpene and esters are considered as the most positive for the "bouquet" of the beer, whereas acids or sulfur compounds bring cheesy or onion flavour [2]. Various factors can affect the concentration of these flavour active compounds. The choice of the hop variety is undoubtedly the most important factor which can drive the aromatic signature of a beer produced with this technique. The influence of the hop variety using dry hopping on the final aromatic perception of beer remains a challenge for brewers.

In this study we have evaluated beers produced with the hop varieties Aramis, Barbe Rouge and Mistral in dry hopping. Using sensory analysis and metabolic profiling we evaluated their respective influence on the beers' aroma and investigated their respective aromatic compound profiles.

Briefly, hop varieties were provided by Cophoudal/Comptoir Agricole (Hochfelden, France) in 2015. Aramis was used as bittering hop (α-acid = 9.6 %) and the other (including Aramis) to do the dry hopping. Brewing experiments were performed in the 50 l pilot brewery of Twistaroma. Beers were then filtered and split into three smaller fermenters (15 l) at 4 °C for dry hopping during eight days with 6 g/l of either Aramis, Barbe Rouge or Mistral hop powder. Beers were bottled immediately after filtration, analyzed by Stir Bar Sorptive Extraction-GC-MS in triplicate by Twistaroma (Table 1, 2 and 3), and sensory evaluated following six criteria: pleasant, floral, fruity, herbaceous, hoppy and spicy by a group of 32 people from INRA Colmar trained to memorize and recognize odours in wine.

The odour activity values (OAVs) of each compound were calculated by dividing the aroma compound concentrations with their perception thresholds. Only the compounds with an OAV greater than 1 were ac-

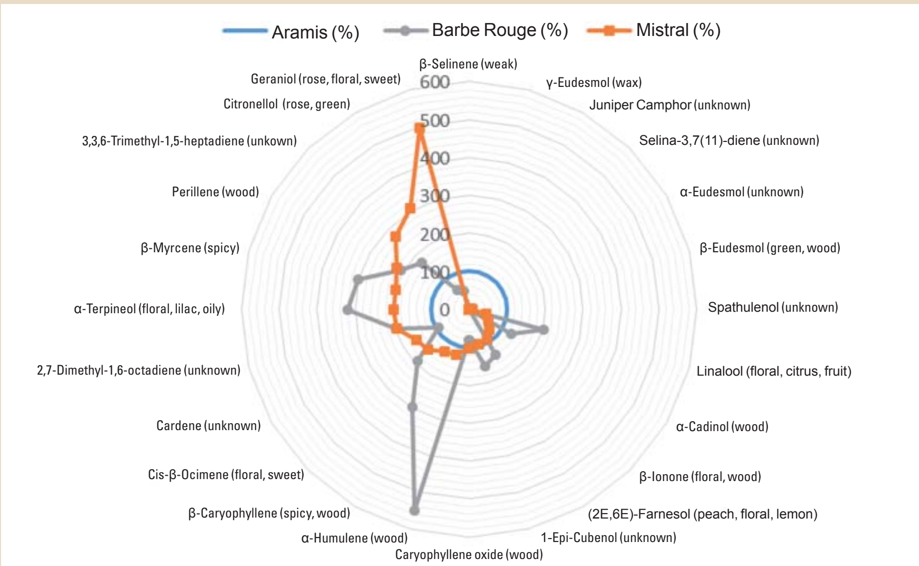

Fig. 1 Spider graph of volatile terpenes (% rel. to Aramis 100 %) in concentration statistically different between Aramis, Barbe Rouge and Mistral beers

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is, Mistral and Barbe Rouge Hopping

TERPENES CONCENTRATION PROFILES (ESTIMATION IN µg/l)

Compounds	Descriptions	Threshold (µg/l)	Concentration (µg/l) (OAV)		
			Aramis	Barbe Rouge	Mistral
Perillene	wood	13 000	0.110	0.230	0.250
Methyl geranate*	floral, green	400	2.31	4.61	4.00
(2E, 6E)-Farnesol*	peach, floral, lemon	80	0.020	0.020	0.010
Cis-β-Ocimene*	floral, herbaceous	1	0.020	0.050	0.040
Geranyl acetate*	rose, sweet	10	ND	ND	0.400
2,7-Dimethyl-1,6-octadiene*	unknown	60	0.480	0.950	0.930
α-Cadinol	wood	1600	0.200	0.250	0.110
α-Eudesmol*	unknown	500	1.200	0.060	0.050
β-Selinene*	spicy, herbaceous	6	0.002	ND	ND
Cardene*	unknown	210	1.130	1.060	1.820
Juniper Camphor*	unknown	500	0.680	ND	ND
Selina-3,7(11)-diene*	unknown	3500	0.002	ND	ND
Spathulenol*	unknown	5	0.220	ND	0.017
Calamenene	spicy	100	ND	0.001	ND
1-Epi-Cubenol	unknown	5	0.150	0.230	0.140
β-Myrcene*	spicy	150	0.430	1.290	0.860
Caryophyllene oxide	wood	3	0.039	0.032	0.040
β-Ionone*	floral, fruit	18	0.124	ND	0.093
α-Humulene*	wood	0.12	0.005	0.030	0.007
β-Eudesmol*	green, wood	10 000	0.979	0.060	0.056
γ-Eudesmol*	sweet, wax	200	0.420	ND	ND
β-Caryophyllene*	spicy, wood	64	0.002	0.007	0.003
α-Copaene*	wood, spicy	6	ND	ND	0.004
γ-Cadinene*	wood	10	ND	0.001	0.001
3,3,6-Trimethyl-1,5-heptadiene*	unknown	18	0.22	0.39	0.61
Terpenol					
Citronellol*	rose, green	5	5.63 (1.1)	3.400	17.39 (3.5)
Linalool*	floral, citrus, fruit	14	67.63 (4.8)	137.62 (9.8)	31.33 (2.2)
α-Terpineol	floral, lilac, oily	250	0.75	2.42	1.49
Geraniol*	rose, floral, sweet	36	4.73	2.33	23.47
Nerol	floral, sweet	50	ND	1.25	2.87

Table 1 *ND: Not detected; * Concentration statistically different between the three beers (p-value<0,05); OAV are mentioned only if higher than 1*

cepted to contribute individually to the beer aroma.

Aromatic Profiles

Terpenes are known to be one of the major contribution of hops to beer aroma, especially in dry hopping beer. Here we show that each beer displays a specific terpene profile. Barbe Rouge beer contained high concentrations of α-humulene (balsamic, wood) and β-caryophyllene (clove, black pepper) while Mistral beer was characterized by geraniol (rose, lychee) and citronellol (rose, green, citrus) (Fig. 1). Aramis beer was defined by richer α, β and γ-eudesmol (green, wood), juniper camphor and selina-3,7(11)-diene content.

The most odour active terpene measured in the three beers produced were deter-

ACIDS, ALCOHOLS, ALDEHYDES, KETONES, PHENOLS AND THIOLS CONCENTRATIONS (ESTIMATION IN µg/l)

Compounds	Descriptions	Td (µg/l)	Concentration (µg/l) (OAV)		
			Aramis	Barbe Rouge	Mistral
Acids					
2-Methyl-2-pentenoic acid	wood	70	142.52 (2)	290.16 (4)	278.94 (4)
Isobutyric acid*	rancid, butter, cheesy	200	523 (2)	1215 (6)	1360 (6)
Isovaleric acid*	rancid, cheesy, acidic	30	368 (12)	797 (26)	868 (29)
Propanoic acid*	pungent, rancid, soy	14	319 (22)	298 (21)	352 (25)
Hexanoic acid	cheesy, rancid, sweaty	2400	119.86	126.63	126.91
Octanoic acid*	fatty, rancid	910	193.24	302.13	451.13
9-Decenoic acid*	fatty, wax	5	ND	7.05 (1)	3.36
Nonanoic acid*	fatty, rancid	unknown	ND	3.09	2.15
Decanoic acid*	rancid, soapy	1500	10.78	23.77	28.02
Dodecanoic acid	metallic, wax	2200	0.03	0.11	0.08
Alcohols					
2-Phenyl Ethanol*	rose, floral, honey	12 500	25 195 (2)	25 607 (2)	27 279 (2)
1-Octen-3-ol*	mushroom, earthy	200	36.03	35.47	ND
Acetol	nutty	1800	68 409 (38)	60 154 (33)	95 355 (53)
Isoamyl alcool*	alcoholic, malty, fusel	65 000	19 632.86	17 508.44	21 626.39
3-Methyl-2-Buten-1-ol	herbaceous	570	127.33	166.78	158.97
Benzene methanol*	sweet, floral, fruit	400	ND	210.71	280.15
1-Octanol	green, floral, rose	900	18.24	22.56	17.49
1-Hexanol*	herbaceous, floral	1100	33.36	60.83	39.37
1-Decanol*	floral, orange, fatty	180	1.49	1.35	ND
2-Tridecanol*	unknown	unknown	0.01	0.01	ND
1-Heptanol*	green, fruit	unknown	27.65	69.12	ND
2-Nonanol*	green, watermelon	unknown	15.3	8.01	6.32
2-Undecanol*	fruit	unknown	1.1600	ND	ND
Aldehydes					
5-Methyl Furfural*	caramel, spicy	60 000	42.31	34.80	72.75
Decanal	green, tallow	6	0.29	0.50	0.32
Furfural*	alkane, sweet, floral	2000	381.54	349.41	934.49
1-Nonanal*	floral, fruit	1	ND	ND	0.72
Furan					
2-Furanmethanol	burnt, sweet	1000	6571.94 (6)	6914 (6)	10 589 (10)
Maltol	caramel, burnt sugar	900	10 341 (11)	7127 (7)	14 927 (16)
2-Methylfuran	unknown	3500	11.61	1.11	16.95
THEASPIRAN*	earthy, geranium	3	ND	ND	0.02
Ketones					
3-Buten-2-one	sweet	1400	1935 (1)	3250 (2)	3369 (2)
2-Heptanone*	fruit, blue cheese, sweet	2000	10.71	18.66	18.60
Methyl isobutyl ketone*	unknown	60 000	ND	550.87	83.23
2-Undecanone	floral, orange	400	2.35	1.94	0.88
3-Methyl-2-butanone	camphor, ether	60 000	56.40	97.60	289.10
2-Decanone*	fruit	190	4.41	2.97	2.70
2-Nonanone*	fruit, green, soapy	38	25.07	ND	ND
2-Hydroxy-2-cyclopenten-1-one*	unknown	3500	911.91	1772.85	ND
Acetone	unknown	400	8840 (22)	13 218 (33)	13 062 (32)
Butyrolactone *	sweet, caramel, fruit	910	8892 (9)	13 359 (14)	7814 (8)
Phenols					
Guaïacol*	burnt, smoky	10	11.59 (1)	4.7	0.0
4-Vinylguaiacol	spicy, clove, smoky	5	79.59 (15)	85.35 (17)	72.93 (14)
2,4-Di-tert-butyl-phenol	phenolic	30	0.038	0.020	0.020
Thiols					
Dimethyl sulfide*	sulfury, cabbage, Truffle	30	2247 (74)	ND	ND
Dimethylsulfoxide*	unknown	unknown	ND	37.127	50.898

*Table 2 ND: Not detected; * Concentration statistically different between the three beers (p-value<0,05); OAV are mentioned only if higher than 1.*

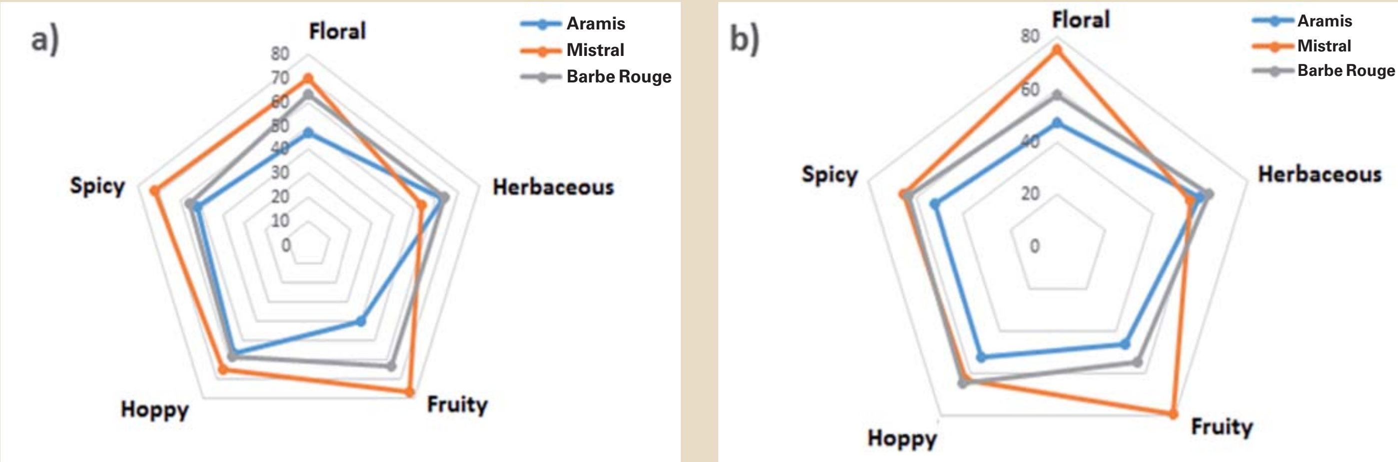

Fig. 2 Spider graph of the rank sum (in %) observed for a) "nose" and b) "mouth" of each hop variety for the studied criterion in beer

mined as linalool (floral, citrus, fruit) and citronellol (rose, green). Takoi et al. [3] described a potential synergistic effect of linalool, geraniol and citronellol accumulation. This phenomenon could explain the citrus aroma enhancement in the three beers. Barbe Rouge contained higher concentration of linalool (138 µg/l) whereas Mistral had higher concentrations of geraniol (23 µg/l) and citronellol (17µg/l) (Fig. 1).

Mistral provided higher concentration of propanoic, isovaleric and isobutyric acids (rancid notes). These three compounds are odour-active in beer and are characteristic of dry hopping [1]. Aramis-derived beer was the less concentrated in detectable acids in our experiment (Table 2).

The most odour-active alcohols detected in our experiment were 2-phenyl ethanol and acetol (Table 2). Acetol concentration was unfortunately badly determined due to the extraction procedure (low affinity with the Stir Bar Sorptive Extraction method) and it was not possible to separate the influence of each hop variety. Nevertheless, in our experiment it was the most odour-active compound in this chemical family. The flavour-active 2-phenylethanol (positive note of rose) was present in similar concentration in the three beers, but could be increased using Mistral for dry hopping (Table 2). For the other alcohol compounds, the influence of each hop can be considered as negligible on the final aroma.

Furfural, 5-methyl furfural and nonanal were influenced by the hop variety used, but their concentrations remained below their respective thresholds and are unlikely to play a role in the final aroma according to our results (Table 2).

Even though furanmethanol and maltol were detected at concentrations higher than their respective thresholds, our study did not show any statistical differences. Hops are unlikely to influence aroma in beer

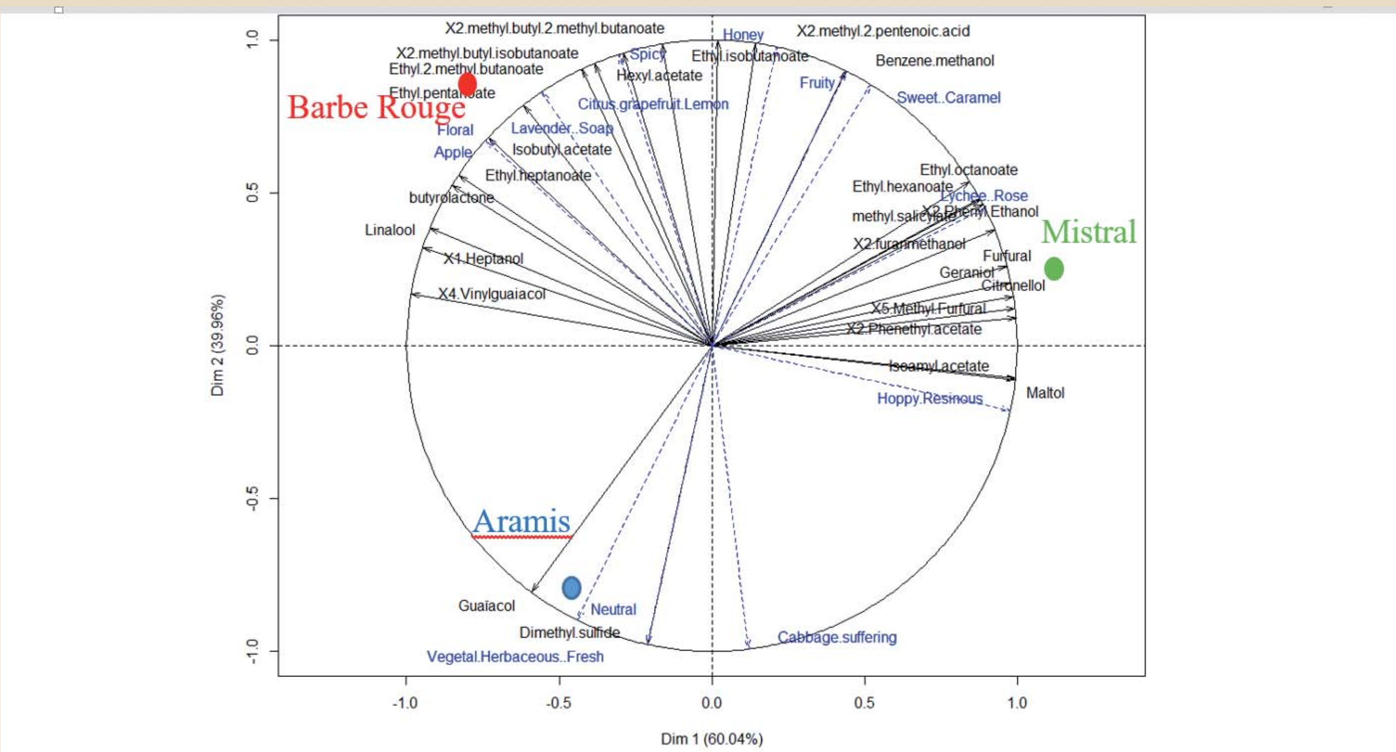

Fig. 3 PCA biplot of sensory attributes and volatile compounds profiling of Mistral, Aramis and Barbe Rouge hops aromatics differences

through furan profiles (Table 2). The three hops studied showed minor ketone variations. Of note only γ-butyrolactone (sweet caramel) was different and odour-active in the beer studied. Barbe Rouge showed the highest concentration of this compound (Table 2).

Only beer produced with Aramis hops contained compounds such as guaïacol (burned, smoked) and dimethyl sulfide (cabbage) (Table 2).

Barbe Rouge showed high ester concentrations compared to Mistral and Aramis beers (Table 3). These esters are considered as positive contributors of the dry hopping process [4]. Due to their strawberry, apple and tropical fruit notes, these esters are probably responsible for the main olfactive contribution of Barbe Rouge to the beer.

Table 4 summarizes all odour-active compounds characterizing each hop variety studied.

Sensory Analysis

A sensory analysis was assessed on the three beers to determine the effect of hop varieties on beer aroma and taste profile. The descriptors/criterions chosen for this analysis were "pleasant", "floral", "fruity", "grass", "hop" and "spicy" both at nose and at mouth (Fig. 2).

At nose, Mistral and Barbe Rouge had the same "pleasant", "floral", "fruity" and "spicy" perception. Both were significantly more "pleasant" and "fruity" than Aramis. At mouth, Mistral was significantly more pleasant and fruity than Aramis and Barbe Rouge (Fig. 2).

Correlation between Volatile Analysis and Descriptive Sensory Analysis

A Principal Component Analysis (PCA) was performed to study the correlation between volatile compound profiles with the sensory descriptors given to the panel during beer tasting (Fig. 3).

ESTERS CONCENTRATIONS (ESTIMATION IN µg/l)

Compounds	Descriptions	Td (µg/l)	Concentration (µg/l) (OAV)		
			Aramis	Barbe Rouge	Mistral
Esters					
Isoamyl acetate*	banana, fruit, sweet	500	3981.24 (8)	3551.83 (7)	4605.6 (9)
Ethyl acetate	fruit, pine apple, sweet	30000	35718.47 (1)	30188.43 (1)	29633.8
Butyl acetate	fruit, floral, thinner	900	20.0	20.9	18.0
Hexyl acetate	fruit, floral, pear	3500	5.0	8.2	6.4
Heptyl acetate*	apricot	190	1.4	3.4	ND
Isobutyl acetate*	fruit, floral, banana	27	66.73 (2)	96.37 (3)	67.15 (2)
2-Phenethyl acetate	floral, rose, honey	515	2627.33 (5)	2535.2 (4)	2940.6 (5)
Ethyl propanoate	fruit, sweet	10	197.64 (19)	239.67 (24)	261.91 (26)
Ethyl butanoate	fruit, sweet, strawberry	400	380.4	389.5	384.2
Ethyl isobutanoate*	fruit, sweet, strawberry	200	79.3	433.81 (2)	302.25 (1)
Ethyl 2-methyl butanoate*	fruit, apple, sweet	6	14.39 (2)	64.02 (10)	33.63 (5)
Ethyl pentanoate*	fruit, apple, floral	900	6.1	8.0	6.4
Ethyl hexanoate*	fruit, green apple, sweet	210	511.92 (2)	545.7 (2)	680.65 (3)
Ethyl 2-hexenoate	fruit	250	1.2	1.7	1.5
Ethyl heptanoate*	fruit, wine	4000	6.9	9.6	6.4
Ethyl octanoate*	fruit, sweet, floral	1,6	40.86 (25)	46.5 (29.1)	62.29 (38)
Ethyl 9-decenoate	fruit	900000	0.2	0.2	0.1
Ethyl nonanoate*	fruit, rose, floral	1200	0.1	0.2	0.2
Ethyl decanoate*	fruit, grape fruit, pleasant	200	0.3	0.7	0.4
Ethyl dihydrocinnamate*	floral, fruit, sweet	30000	1.7	1.2	1.9
Ethyl cinnamate	honey, floral	180	6.1	6.7	5.5
Hexyl isobutanoate*	unknown	30	0.0	2.0	0.0
2-Methylpropyl propanoate*	unknown	7500	13.3	28.3	11.9
2-Phenylethyl butanoate*	musty	14000	4.5	2.5	3.1
2-Phenethyl hexanoate*	fruit, unknown	10000	1.5	0.0	2.9
2-Phenylethyl octanoate	unknown	3000	0.02	0.1	0.1
3-Methyl-ethyl-butanoate*	sweet	10	8.9	12.15 (1)	8.1
2-Methyl butyl 2-methyl butanoate*	unknown	570	1.2	7.5	6.2
2-Methyl butyl isobutanoate*	tropical note	78	135.28 (1)	753.06 (9)	452.65 (5)
1-Methylbutyl propanoate*	unknown	5	53.45 (10)	0.0	51.46 (10)
1-Butanol 2-methyl propanoate*	unknown	20	ND	96.64 (4)	ND
Isobutyl isobutanoate*	fruit, strong	200	159.8	659.44 (3)	328.51 (1)
Isobutyl 2-methylbutanoate*	sweet, herbal	7500	3.4	19.2	11.5
Methyl salicylate*	sweet, minty, spicy	40	27.1	29.8	41.78 (1)

Table 3 *ND: Not detected, * Concentration statistically different between the three beers (p-value<0,05); OAV are mentioned only if higher than 1.*

Volatile compounds previously identified were selected according to both their concentrations and olfactory activities in beers. The descriptors used to perform the PCA were quantified by counting the number of times they were cited during the sensorial test by the panel of 32 judges.

The main descriptors for Mistral are "lychee" and "rose". PCA and previous statistical analysis (Table 2) showed that geraniol and citronellol are typical of this hop variety highlighting the sensory analysis suggesting that these compounds may be involved in the floral, rose and lychee perception of this beer. In beer produced with Barbe Rouge, the main descriptors surveyed were "citrus/lemon", "lavender/soap" and "apple". While the two first descriptors are linked with the linalool content, the latter, "apple", may be related to the presence of ethyl pentanoate and ethyl-2-methyl butanoate [5] in this variety (Table 4).

Finally, "cabbage-flavoured" aroma, stronger in Aramis than in Barbe Rouge or Mistral, can be linked to the presence of dimethyl sulfide [6].

Conclusion

Aramis, Barbe Rouge and Mistral, three Alsatian hop varieties, were used in dry hopped beers. The resulting aromatic profiles were then compared using aromatic and sensorial analysis. Results indicate that the choice of hop variety has a major influence on beer character. Mistral stands out from the two other hops through its terpene composition with the trio geraniol/citronellol/linalool which provide rose floral notes and lychee fruity notes. Barbe Rouge is characterized by its typical esters composition bringing notes of red fruits such as strawberry and exotic fruits to the beer. Finally, Aramis shows a powerful aromatic signature combining key aromas of Mistral (terpenes) and Barbe Rouge (esters) present in concentration lower than both of these hops. ■

Acknowledgments

The author would like to express his deep appreciation to Dr Valentin Le Douce.

VOLATILE MARKERS OF THE HOP VARIETY STUDIED ...

... (OAV>1 and concentration statistically different between Aramis, Barbe Rouge and Mistral beers)

Beers	Typical compounds	Odours
Aramis beer	2-Phenethyl butanoate	Cheese, liquor, wine
	Butyl acetate	Fruit, floral
	Guaiacol	Burnt, smoked
	Dimethyl sulfide	Cabbage
Barbe Rouge beer	Linalool	Floral, citrus, fruit
	Ethyl isobutanoate	Fruit, sweet, strawberry
	2-Methylbutyl-2-methyl butanoate	Fruit
	Ethyl-2-methyl butanoate	Apple, strawberry
	2-Methylbutyl isobutanoate	Tropical notes
	Ethyl heptanoate	Fruit, wine
	1-Octanol	Green
	Butyrolactone	Caramel, fruit
Mistral beer	Geraniol	Rose, floral, sweet
	Citronellol	Rose, green
	2-Phenethyl acetate	Fruit, rose, honey
	2-Phenethyl hexanoate	Fruit
	Ethyl hexanoate	Green apple
	Ethyl octanoate	Floral, sweet
	Methyl salicylate	Sweet, minty, spicy
	2-Furanmethanol	Burnt, sweet
	2-Heptanone	Blue cheese, fruit
	3-Buten-2-one	Sweet
	Isovaleric isobutyric acids	Rancid

Table 4

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Barbe Rouge

The Hop Revolution

HOP FRANCE
by Comptoir agricole