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What is unique in Belgian dry-hopped beers?

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Introduction

Renowned for a long time around the world for its unique dry-hopped Trappist Beer, Belgium has been also developing other dry-hopped beers, often with a nice equilibrium between bitterness, astringency, fruity flavors and green notes. New beers are constantly arriving on the market and traditional breweries are developing recipes to follow this trend. Today, Belgium has more than 30 different labels of dry-hopped beers. Even though dry-hopped beer is not considered a style, the addition of hop during the late stages of the brewing process (in presence or not of yeasts) brings singular characteristics to the beer¹. Free² and bonded polyfunctional thiols^{3,4}, polyphenols and unisomerized bitter components of hop can significantly modify the flavor profile of such beers⁵. The aim of this work was to investigate, by physicochemical and sensorial analyses, the main characteristics of dry-hopped Belgian beers.

The beers

Most of the beers here investigated have been kindly provided by brewers: Brasserie d'Orval – Orval (A), Brasserie de Bastogne – Bastogne Pale Ale (B) and La Trouffette Blonde (C), Duvel Moortgart Brewery – Vedett Extra Ordinary IPA (D) and Duvel Triple Hop 2015 (E), Brasserie de Jandrain-Jandrenouille – IV Saison (F) and V Cense (G), InBev Belgium – Leffe Royale Cascade IPA (H), Leffe Royale Mapuche (I) and Leffe Royale Mount Hood (J), Brasserie d'Achouffe – Houblon Chouffe (K), Brasserie de la Senne – Taras Boulba (L), Brasserie St-Feuillien – St. Feuillien Saison (M) and St. Feuillien Grand Cru (N), Brasserie de Ranke – Guldenberg (O) and Brasserie artisanale de Namur – Houppé (P). The others have been bought in local markets: Duvel Triple Hop 2011 (Q), Duvel Triple Hop 2012 (R), Duvel Triple Hop 2013 (S), Duvel Triple Hop 2014 (T) and Duvel Triple Hop 2016 (U).

Apparent and original extracts and alcohol content were analyzed using an Alcozyler Beer Analyzing System DMA 4500 M. pH, bitterness, total polyphenols, total flavanoids and color were analyzed following the Analytica-EBC (European Brewery Convention) guide, 2002 (Table 1).

Table 1. Results of classical analyses of dry-hopped Belgian beers.

Beer	Alcohol content (% ABV)	Original extract (°P)	Apparent attenuation (°P)	pH	Color (°EBC)	Total polyphenols (mg/L)	Total flavanoids (mg/L)	Degree of polymerization	Bitterness (°EBU)
A	6.6	16.5	97.7	4.29	15.5	81.2	44.1	1.8	25.2
B	5.1	13.2	77.6	4.35	13.5	170.2	52.3	3.3	42.2
C	6.1	15.1	81.2	4.42	11.5	244.8	52.6	4.7	34.6
D	5.4	13.5	81.4	4.4	14.5	171.4	47.7	3.6	36.1
E	9.3	19.8	93.6	4.05	6.2	292.5	73.7	4.0	40.9
F	5.4	12.4	90.0	4.45	12.5	166.5	35.6	4.7	40.3
G	6.0	13.4	89.8	4.54	31.5	155.4	27.0	5.8	30.4
H	7.2	15.5	93.7	4.42	10.0	119.5	25.5	4.7	31.8
I	7.2	15.6	93.0	4.36	16.5	132.0	27.6	4.8	28.8
J	6.8	17.6	78.3	4.37	43.5	137.1	28.2	4.9	28.5
K	8.3	18.4	90.1	4.32	11.0	341.3	71.8	4.8	44.1
L	4.4	10.5	85.3	4.45	5.0	333.1	66.7	5.0	57.9
M	6.6	15.6	85.2	4.46	14.5	300.9	54.4	5.5	25.7
N	9.1	20.6	88.7	4.5	8.3	255.6	53.0	4.8	29.8
O	7.4	18.8	79.7	4.44	14.5	360.6	61.1	5.9	33.8
P	7.4	17.8	84.1	4.03	29.0	287.6	58.3	4.9	42.3
Q	9.1	19.6	93.4	4.05	5.5	221.4	65.3	3.4	33.1
R	9.3	19.7	94.2	4.04	6.0	239.4	69.3	3.5	35.2
S	9.3	19.6	94.2	4.01	6.0	235.3	69.8	3.4	32.0
T	9.1	19.2	94.8	4.03	6.2	250.9	72.7	3.5	37.0
U	9.4	19.7	95.2	4.13	5.7	225.1	73.9	3.0	32.0

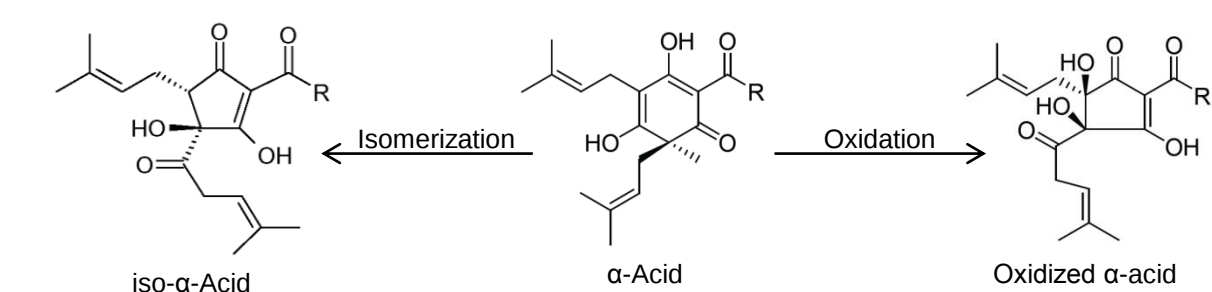
Table 2 shows how wide is the diversity among Belgian dry-hopped beers. A and L were pointed as exhibiting the extreme values.

Table 2. Range between the physicochemical lowest and highest values.

Characteristic	Min	Range	Max
Alcohol content (% ABV)	L	4.4 – 9.4	U
pH	S	4.01 – 4.54	F
Color (°EBC)	L	5.0 – 43.5	J
Original extract (°P)	L	10.5 – 20.5	N
Apparent extract (°P)	A	0.4 – 3.8	J
Total polyphenols (mg/L)	A	81.2 – 360.6	O
Total flavanoids (mg/L)	H	25.3 – 73.9	U
Degree of polymerization	A	1.8 – 5.9	O
Bitterness (°EBU)	A	26.5 – 58.3	L
Iso-α-acids (mg/L)	J	10.9 – 46.4	L

iso-α-Acids

As depicted in Figure 2, no correlation was found between HPLC data and perceived bitterness, although N and K presented the highest values in both methods.

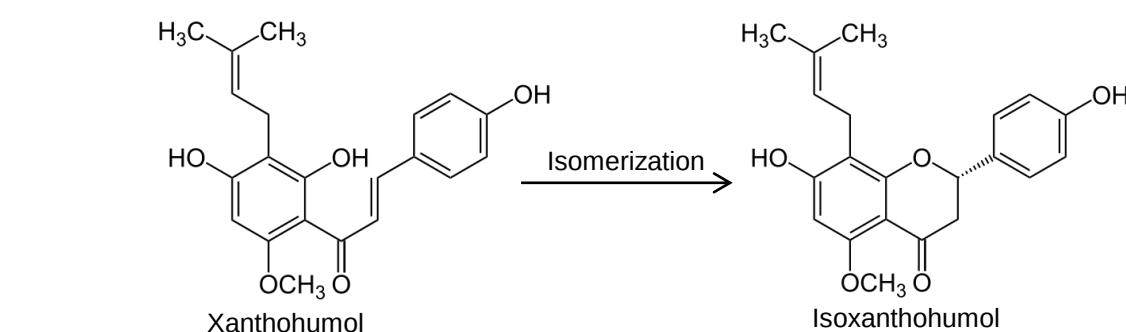


Oxydized α acids

Beer α-acids revealed to mainly come from dry hopping. Oxidized humulones such as humulinones are rare in late hopping beers but frequently found in dry-hopped beers (Figure 4).

Isoxanthohumol and xanthohumol

Isoxanthohumol is known to be produced in the kettle from hop xanthohumol. As shown in Figure 4a, significant amounts of xanthohumol can still be quantified in most dry-hopped beers. Yet no correlation was evidenced between α-acids and xanthohumol contents for our dry-hopped beers (Figure 4b).



Bitterness

iso-α-Acids, α-acids, xanthohumol and isoxanthohumol were isolated from dry-hopped beers by solid phase extraction and analyzed by RP-HPLC-UV. Each compound or group of compounds was analyzed at the recommended wavelength (Figure 1). Standards for iso-α-acids (ICS-2) and α-acids (ICE-3) were purchased from Labor Veritas (Zurich, Switzerland). Xanthohumol and isoxanthohumol were generously provided by Hopsteiner (Mainburg, Germany).

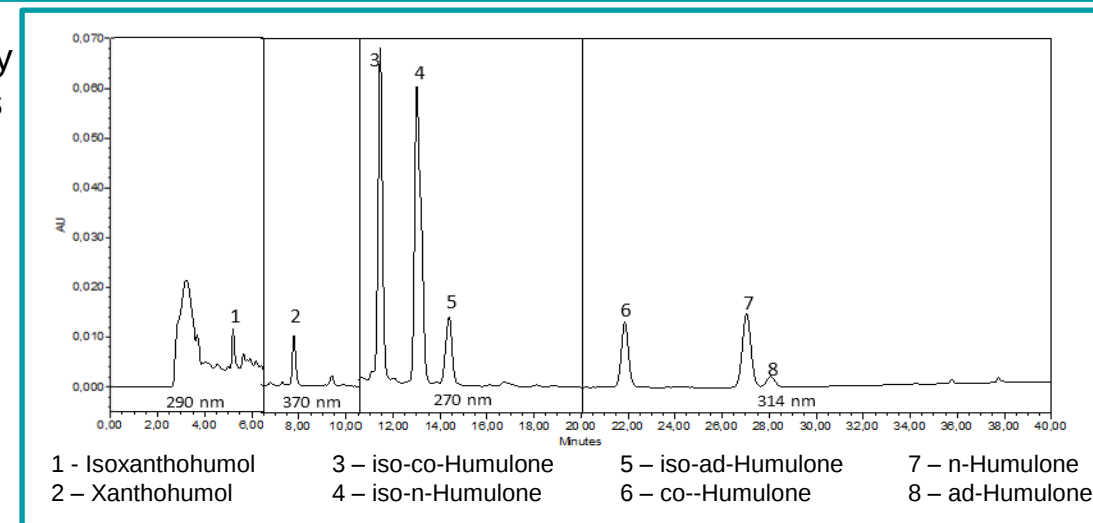


Figure 1. Chromatogram of the beer F divided by wavelength according to target compounds

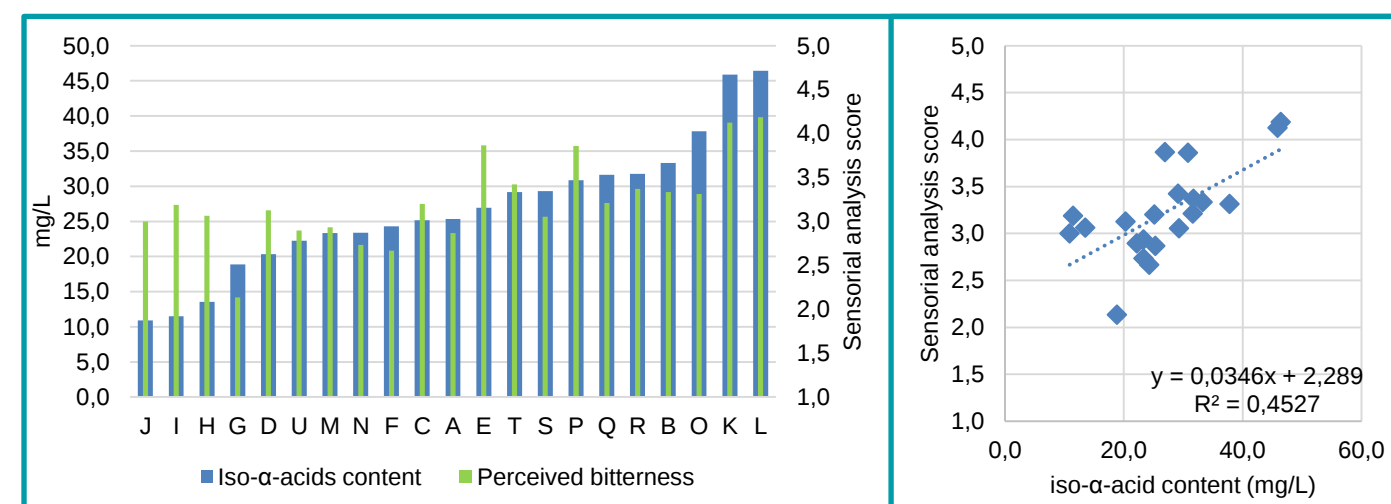


Figure 2. iso-α-Acids content and perceived bitterness of analyzed dry-hopped Belgian beers (left) and their correlation (right).

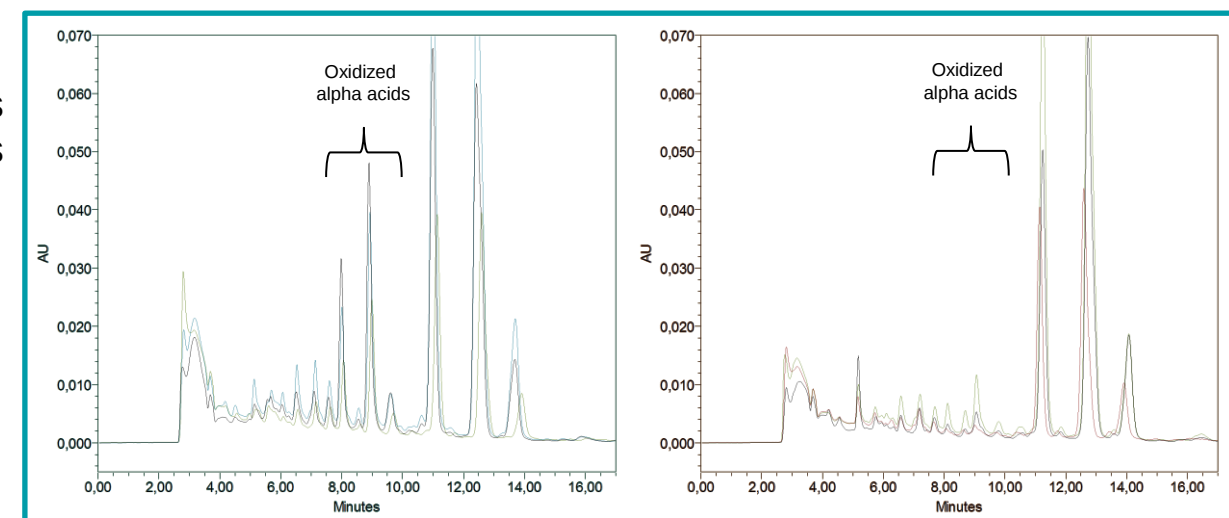


Figure 3. Chromatograms at 270 nm of 3 different dry-hopped (left) and 3 late hopping Belgian beers (right).

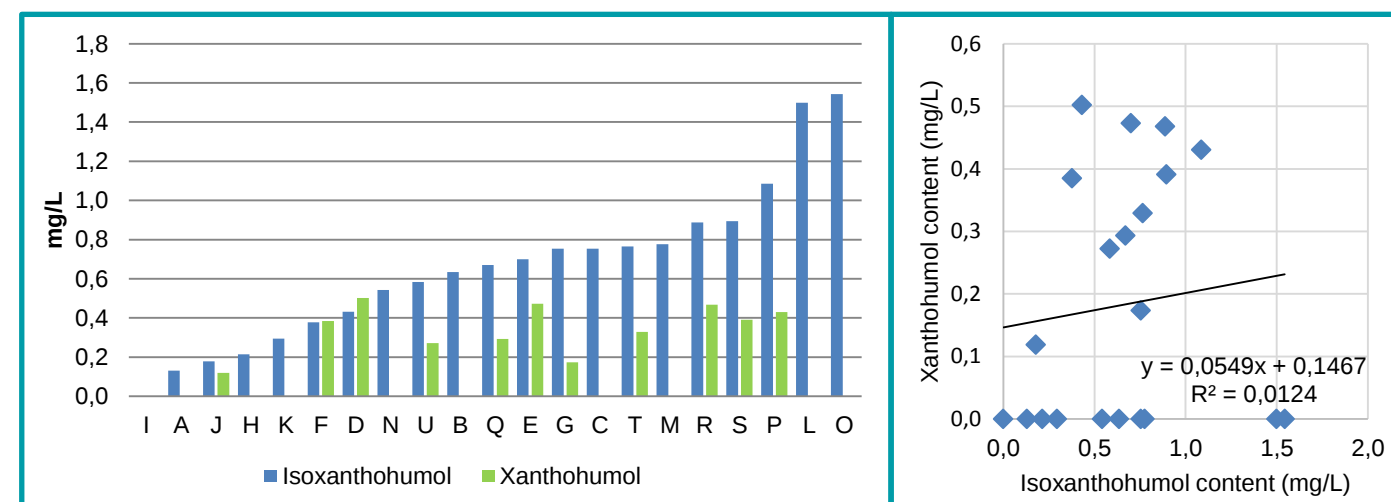


Figure 4a. Isoxanthohumol and xanthohumol content in analyzed dry-hopped Belgian beers

Figure 4b. Correlation between isoxanthohumol and xanthohumol content.

Aroma

Sensorial analysis

Nine trained panelists scored several beer attributes on a scale of 0 to 4 (0 means absence and 4 means strong perception). No specific flavor profile was here evidenced for dry-hopped beers, although fruity and herbal notes were often key flavors. No relation between bitterness and hop aroma intensity was found.

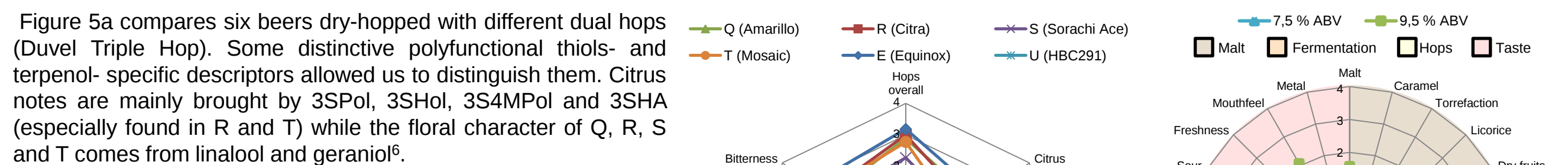


Figure 5a compares six beers dry-hopped with different dual hops (Duvel Triple Hop). Some distinctive polyfunctional thiols- and terpenol- specific descriptors allowed us to distinguish them. Citrus notes are mainly brought by 3SPol, 3SHol, 3S4MPol and 3SHA (especially found in R and T) while the floral character of Q, R, S and T comes from linalool and geraniol⁶.

Figure 5b compares two beers (7.5 and 9.5 % ABV) dry-hopped in the same way. A higher alcohol content increases the solubility of hydrophobic compounds responsible for pleasant citrus and floral notes while green hop descriptors are highly perceived in the 7.5 % ABV beer.

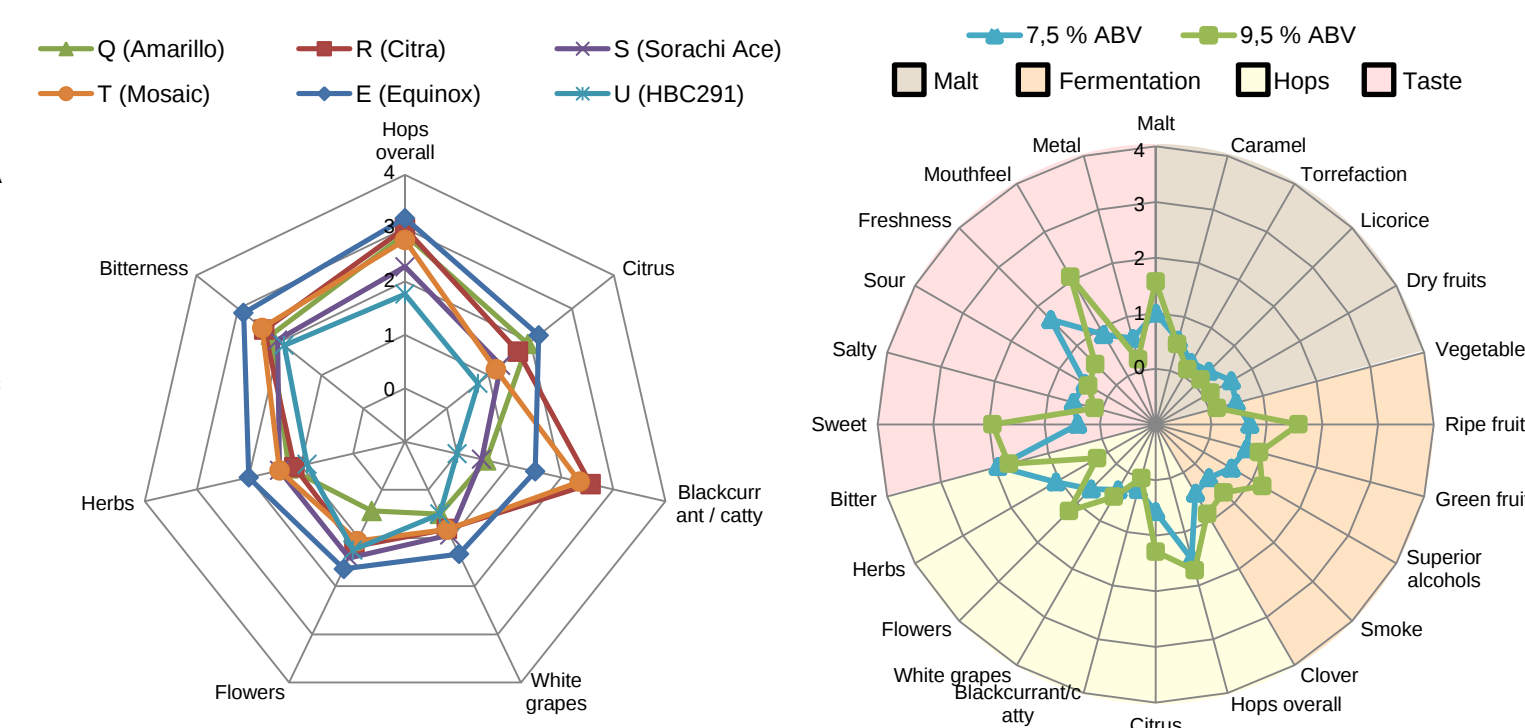


Figure 5a. Sensorial analysis of six beers dry-hopped with different dual hops (Duvel Triple Hop).

Figure 5b. Sensorial analysis of two beers with different alcohol contents, dry-hopped with the same variety.

Polyfunctional thiols

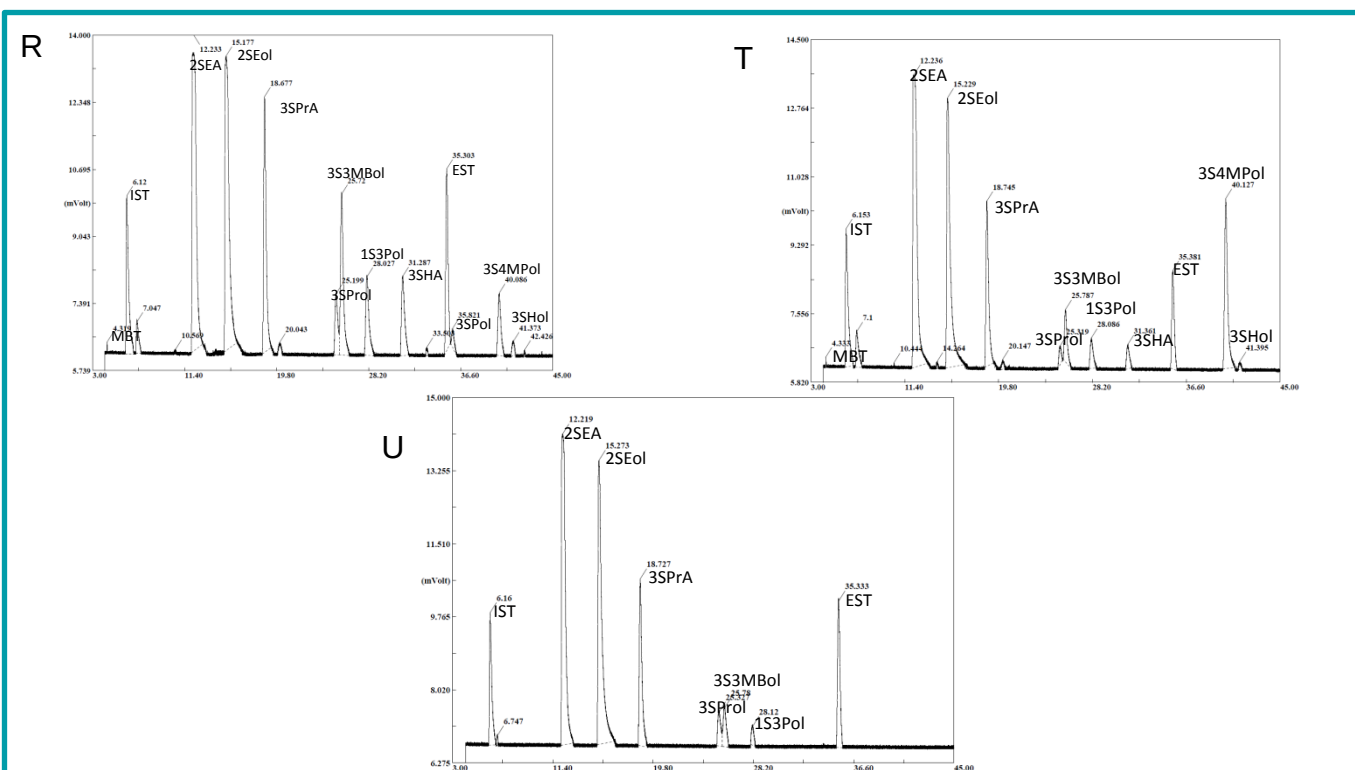


Figure 6. GC-PFPD chromatograms of pMB extracts issued from beers R, T and U.

The here above PFPD-chromatograms confirm the key role of polyfunctional thiols in R, T and U.

Terpenoids

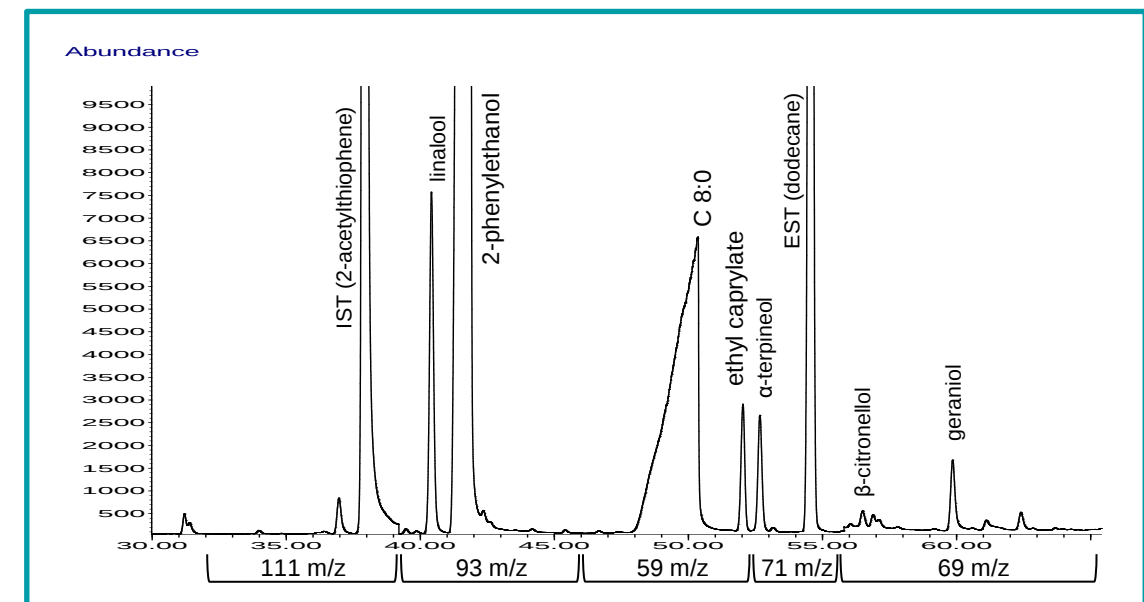


Figure 7. GC-MS-chromatogram in SIM mode of a SAFE extract issued from beer N.

The here above MS-chromatogram confirms the key role of terpenoids in N.

Conclusion

Our results confirmed that Belgian dry-hopped beers do not constitute a single beer style (wide range of colors, alcohol contents and measured bitterness). Yet most of them are characterized by an exceptional well balanced aroma profile, not too bitter or astringent. Beside terpenoids and polyfunctional thiols, the dry-hopping process brings additional α-acids, humulinones and xanthohumol to the beer, which can impact their flavor in a singular way.

References

[1] Collin et al., Cerevisia, 2012, 36, 119-124; [2] Gros et al., J. Agric. Food Chem., 2011, 59, 8853-8865; [3] Gros et al., J. Inst. Brew., 2013, 119, 221-227; [4] Thi Thu et al., J. Am. Soc. Brew. Chem., 2015, 73, 61-70; [5] Algazzali and Shellhammer, J. Am. Soc. Brew. Chem., 2016, 74, 36-43; [6] Kankolongo Cibaka et al., J. Agric. Food Chem., 2015, 63, 3022-3030.

Acknowledgement

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