ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/321964807

Systematic Analysis of Behaviour of Hop-Derived Monoterpene Alcohols During Fermentation and New Classification of Geraniol-Rich Flavour Hops

Article in BrewingScience · December 2017

DOI: 10.23763/BRSC17-17TAKOI

CITATIONS
3

READS
192

1 author:

Kiyoshi Takoi
Sapporo Breweries

46 PUBLICATIONS 417 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Identification and characterization of unique flavor compound contributing to the varietal aroma of SORACHI ACE hop View project

Analysis of synergy among hop-derived flavor compounds View project

All content following this page was uploaded by Kiyoshi Takoi on 12 March 2019.

The user has requested enhancement of the downloaded file.

K. Takoi, Y. Itoga, K. Koie, J. Takayanagi, T. Kaneko, T. Watanabe, I. Matsumoto and M. Nomura

Systematic Analysis of Behaviour of Hop-Derived Monoterpene Alcohols During Fermentation and New Classification of Geraniol-Rich Flavour Hops

In this study, hop-derived monoterpene alcohols (linalool, geraniol, β-citronellol, nerol, and α-terpineol) and their behaviour during fermentation have been focused on. Total 42 hop varieties were compared. As a result, it was suggested that a group of geraniol-rich 'Flavour hop' varieties, which could generate a large amount of β-citronellol to finished beer, could be furthermore classified into two types, 'free geraniol dominant hops' and 'geraniol precursor dominant hops'. 'Free geraniol dominant hops' mainly contain free geraniol at high levels and subsidiary geraniol precursors. Most of 'geraniol-rich hops' was classified into this type, for example Motueka, Bravo, Cascade, Citra, Mosaic, Sorachi Ace, 0612B and so on. 'Geraniol precursor dominant hops' might mainly contain geraniol precursors at high levels and subsidiary free geraniol, for example, Vic Secret, Comet, Hallertau Blanc, Polaris, Amarillo, HBC366, and Summit.

Descriptors: beer, hop, varietal aroma, flavour compounds, linalool, geraniol, β-citronellol

A preliminary report of some of this work was given at the 35th Congress of the European Brewery Convention, Porto, Portugal, 24-28 May, 2015.

1 Introduction

In recent times, new types of hops, so-called 'Flavour Hops' [14, 24, 32], have been bred and widely used for craft beers all around the world [1, 11, 24, 27–29, 40]. These hops impart very characteristic 'Varietal Aroma', for example citrus-like and/or exotic fruit-like (tropical) flavors, to finished beer. Therefore, beer/hop researchers have been interested in key flavor compounds contributing to such varietal aromas. We have focused on certain 'flavor hop' varieties, for example Bravo, Cascade, Citra, Mosaic and Nelson Sauvin, and revealed the contribution of monoterpene alcohols and volatile thiols to the hop-derived varietal aromas, the behavior of these compounds during beer production and the mechanism of varietal aroma formation based on the synergy among various flavor compounds [43–50].

https://doi.org/10.23763/BrSc17-17takoi

Authors

Kiyoshi Takoi, Ichiro Matsumoto, Masahiro Nomura, Product & Technology Innovation Department, Sapporo Breweries Ltd, Shizuoka, Japan; Yutaka Itoga, Koichiro Koie, Bioresources Research & Development Department, Sapporo Breweries Ltd, Hokkaido, Japan; Junji Takayanagi, Takeshi Kaneko, Takayuki Watanabe, Frontier Laboratories of Value Creation, Sapporo Breweries Ltd, Shizuoka, Japan; corresponding author: kiyoshi.takoi@sapporobeer.co.jp

Hop-derived monoterpene alcohols (linalool, geraniol, β-citronellol, nerol, and α-terpineol) have been investigated by many researchers for a long time [4–9, 13, 15–21, 23–24, 26, 31–38, 40–41, 46-50]. Monoterpene alcohols are more hydrophilic and easier to retain in wort and beer than terpene hydrocarbons, for example β-myrcene. In the 1980s, several researchers reported that beer made from a particular hops, for example Cascade, contained not only linalool but also geraniol and β-citronellol [23, 26, 33]. In these reports, conversion from geraniol to β-citronellol during fermentation had been observed. In the 2000s, the biotransformation pathway of monoterpene alcohols facilitated by brewing yeast has been proposed, firstly based on the result of model fermentations each containing monoterpene alcohols. Geraniol could be mainly transformed to β-citronellol and adjunctively to linalool. Nerol could be converted to linalool and α-terpineol. Part of linalool could be cyclized to α-terpineol [17–18]. It has also been reported that geraniol could be used for ergosterol biosynthesis [52]. Therefore, geraniol showed a drastic decrease during the growth phase, during the first 2–4 days. In model fermentation, a part of geraniol converted to β-citronellol only during this period, because most of geraniol was consumed in this period. In addition, the total amount of monoterpene alcohols gradually decreased during fermentation [17–18]. This pathway was verified by fermentations of beers made with geraniol-rich hop, for example Citra. As a result, in general, the geraniol drastically decreases during first 3 days of fermentation. The β-citronellol was almost absent in hop and wort and gently increased during total fermentation period [46–48].

In the first 3 days of fermentation, the behaviors of geraniol and β-citronellol in the hopped beer were similar to those in model solution. Free geraniol drastically decreased and a part of free geraniol was converted to β-citronellol. On the other hand, β-citronellol in the hopped beer increased in not only the first 3 days but also the storage period, in which the level of free geraniol remained flat [46–48]. Several researchers have reported the occurrence of geranyl esters [7–8, 23, 26, 49], for example geranyl acetate, and glycosidically-bound geraniol precursors [2, 10, 16, 22, 25, 35–36, 46] as possible geraniol precursors. In the fermenting beer, there are several enzymes having releasing activities of free geraniol from possible geraniol precursors, for example esterase activities for geranyl esters and glucoside hydrolase activities for glycosidically-bound precursors [3, 35, 42, 46]. It is assumed that β-citronellol could formed from both free geraniol and such precursors in the storage period. In addition, it was reported that 'Old Yellow Enzyme' derived from yeast could catalyzed the conversion from geraniol to β-citronellol [39, 41, 53]. Based on various recent researches, a biotransformation pathway of monoterpene alcohols derived from hops is summarized as figure 1.

In the viewpoint of sensory chemistry, it was found that there was an additive effect among linalool, geraniol, and β-citronellol [46], and that the flavour impression became lime-like (citrus) by coexistence of these three monoterpene alcohols. Therefore, geraniol metabolism facilitated by yeast is important for the citrus flavor in beer [47]. The concentration of geraniol and β-citronellol in finished beer could be enriched depending on the initial geraniol content in the wort by using geraniol-rich hop [46–48]. In addition, geraniol contents in finished beer increased by delaying the timing of hop-addition, while the yeast growth phase was avoided. On the other hand, the β-citronellol contents in the finished beers made with the same hop variety were present at almost the same levels, regardless of the timings of the hop addition [48]. It is thought that these results are useful for controlling the flavor of hopped beer.

From comparison of the composition of monoterpene alcohols in various hops, linalool is contained in all hops. β-citronellol is at trace levels in all hops. However, geraniol is considered to be more variety-specific than linalool. For example, European hop varieties, Hallertauer Tradition, Hallertauer Magnum, Saaz and so on, contain very small amounts of geraniol and the U.S. hop varieties, including Apollo, Amarillo, Bravo, Cascade, Citra, Mosaic, and others, often contain large amounts of geraniol [6, 23, 26, 37–38, 46–48].

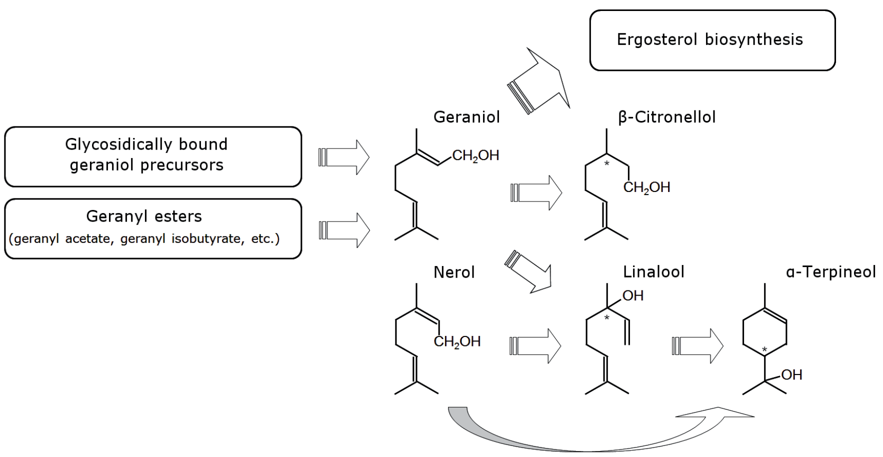

Fig. 1 Biotransformation pathway of monoterpene alcohols by brewing yeast (On the basis of ref. 3, 7-8, 17-18, 23, 39, 41-42, 46-48, 52-53)

In this study, monoterpene alcohols (linalool, geraniol, β-citronellol, nerol, and α-terpineol) during total fermentation period were analysed, and behaviours of hop-derived monoterpene alcohols among total 42 hop varieties were compared.

2 Materials and methods

2.1 Hop raw materials

Saaz from Czech Republic (type 90 pellet). Hallertauer Tradition, Comet, Hallertau Blanc, Hüll Melon, Mandarina Bavaria, and Polaris were grown and pelletized in Germany (type 90 pellet). Aramis, Barbe Rouge, Mistral, and Triskel were bred and grown in France (type 90 pellet). Furano Beauty, Furano No. 18, 9702A, 9803A, and 0612B were bred and grown in Japan (Bioresources Research & Development Department, Sapporo Breweries, Ltd.) (hop powder). Galaxy and Vic Secret were produced in Australia (type 90 pellet). Motueka, Nelson Sauvin, Pacific Jade, Rakau, Riwaka, Southern Cross, Wai-iti, and Waimea were harvested and pelletized in New Zealand (type 90 pellet). Apollo and Bravo were harvested in the U.S. in 2008 (hop powder) and 2010 (type 90 pellet). Cascade was grown in the U.S. in 2007 (type 90 pellet) and 2008 (hop powder).Citra was bred grown in the U.S. in 2007 and 2008 (type 90 pellet). Amarillo, Chinook, Glacier, HBC366, Mosaic (formerly named as HBC369), Mt. Hood, Simcoe, Sorachi Ace and Summit were harvested in the U.S. (hop powder). Nugget was grown in the U.S. (type 90 pellet). Crop years of all hops are summarized in table 1 and 2.

2.2 Pilot-scale brewing

Beers were made with the same recipe according to the standard method of the Production & Technology Development Centre, Sapporo Breweries, Ltd. Briefly, the wort was prepared using commercially available malts (or malts and 33 % adjuncts (starch, corn and rice)) and hops in 100-L or 400-L scale pilot apparatus. Boiling period was 90 min. For prevention of over boiling, HHT hop was added at the beginning of boiling (0.2 g of hop/L). Cooled wort was collected to fermentation tanks (30 L/tank) and medium bottles (900 ml/bottle). For hop-flavouring, 24.8 g of hop was added to each bottle and was autoclaved at 105 °C for 5min. After cooling, the hop-flavoured wort was mixed with 30 L of wort in each fermentation tank. This condition was corresponding to that of the late-hopping with 0.8 g of hop/L. Subsequently, the fermentation was started by adding 15.0 x 10^6 cells/ml lager yeast (brewery collected; *Saccharomyces pastorianus*) to the wort. The temperature of the fermentation was maintained at 10–12°C (primary fermentation). After transferring the fermented wort to another storage tank under a CO_2 atmosphere, the maturation was carried out at 13 °C for 8 days, then at 0 °C for 2–3 weeks. Filtration and bottling were done using the pilot-scale equipment under anti-oxidative conditions.

Table 1 **Comparison of Monoterpene Alcohols (linalool, geraniol, and β-citronellol) (µg/L) during Fermentation of Late-Hopped Beer: area, grown area; rp, repeating trial using same crop sample; ref, reference number (previously reported data); F., primary fermentation; 3d, 3 days; S., storage; 1w, 1 week**

					linalool (µg/L)					geraniol (µg/L)					β-citronellol (µg/L)				
variety	**area**	**crop**	**rp**	**ref**	**wort**	**F. 3d**	**F. end**	**S. 1w**	**beer**	**wort**	**F. 3d**	**F. end**	**S. 1w**	**beer**	**wort**	**F. 3d**	**F. end**	**S. 1w**	**beer**
Saaz	CZ	2008			39,1	28,8	21,1	20,2	19,4	4,6	3,3	2,4	3,3	3,8	0,2	1,7	1,7	4,8	6,1
Hallertauer Tradition	GER	2007		46	53,5	40,8	30,2	27,3	30,9	3,1	2,4	2,3	2,2	2,3	0,3	1,0	1,1	1,2	1,6
Hallertauer Tradition	GER	2009	#1		134	120	86,9	79,8	87,0	4,9	4,0	3,4	3,6	4,3	0,2	1,3	1,4	2,5	3,7
Hallertauer Tradition	GER	2009	#2		127	101	78,9	81,4	64,5	4,7	3,8	3,4	5,0	8,7	0,2	1,6	1,9	3,5	3,9
Comet	GER	2014			28,9	25,4	21,2	22,2	24,1	21,8	16,4	19,2	24,3	27,8	0,2	4,6	6,3	19,3	25,7
Hallertau Blanc	GER	2012			46,6	44,3	37,9	36,1	40,8	23,4	13,2	13,7	17,7	21,0	0,2	5,4	7,0	19,7	28,9
Huell Melon	GER	2012			29,4	24,6	21,0	20,1	22,5	24,1	6,7	5,7	7,3	8,7	0,4	3,4	3,8	9,6	14,4
Mandarina Bavaria	GER	2012			42,4	37,0	31,3	30,7	34,5	32,8	8,4	5,6	7,4	9,6	0,3	4,6	4,0	10,6	16,3
Polaris	GER	2012			38,3	55,6	45,3	44,2	50,2	20,6	20,8	18,4	27,6	35,5	0,4	9,6	11,1	27,1	40,1
Aramis	FR	2013			45,8	32,9	31,5	29,9	33,2	8,2	2,0	2,6	2,4	3,2	0,2	0,7	1,1	2,4	4,1
Barbe Rouge	FR	2013			96,0	94,6	78,0	75,5	82,5	12,9	3,5	3,1	4,6	5,6	0,2	1,4	1,5	3,9	6,4
Mistral	FR	2015			32,9	24,6	21,2	21,3	21,8	43,7	7,2	6,6	8,6	9,3	0,2	2,9	3,0	9,0	11,8
Triskel	FR	2013			57,5	40,1	38,1	42,3	40,9	9,5	2,6	3,8	4,5	4,5	0,4	0,9	1,9	3,8	5,8
Furano Beauty	JP	2009			281	232	186	169	173	88,5	29,8	20,7	20,2	19,6	0,9	12,2	11,1	15,7	17,2
Furano No. 18	JP	2009			88,0	78,4	58,4	56,7	62,5	96,3	22,5	12,2	14,6	15,1	0,6	11,2	7,3	14,5	18,5
9702A	JP	2007		46	160	136	98,6	85,8	99,5	11,6	6,1	5,3	4,7	5,1	1,3	3,0	2,5	2,7	4,2
9803A	JP	2007		46	88,0	72,6	53,4	46,2	53,7	27,2	8,5	6,0	5,9	6,2	1,2	3,8	3,2	4,0	5,4
0612B	JP	2009			152	133	95,7	90,4	98,8	334	73,2	36,4	38,2	38,1	0,3	39,5	23,2	37,6	48,6
Galaxy	AUS	2013			56,9	52,5	45,7	44,8	45,4	18,3	9,9	10,7	14,9	14,8	0,1	3,0	3,9	10,2	13,5
Vic Secret	AUS	2014			27,9	24,2	24,9	23,0	24,0	2,9	5,5	6,7	9,5	8,4	0,2	4,1	7,3	11,2	22,2
Motueka	NZ	2010			116	101	80,2	78,0	76,8	132,0	28,8	21,1	23,1	25,1	0,5	14,4	11,7	17,8	22,4
Nelson Sauvin	NZ	2007			66,2	56,6	42,0	37,9	40,4	19,2	8,4	7,7	10,9	13,2	0,2	3,9	4,7	10,4	14,5
Pacific Jade	NZ	2010			88,5	83,4	64,6	61,6	63,0	22,7	11,4	9,8	11,3	12,3	0,5	4,0	4,1	5,4	7,2
Rakau	NZ	2012			84,9	54,3	39,8	31,0	29,1	63,2	5,0	4,6	4,3	4,7	2,0	2,8	3,0	5,8	6,7
Riwaka	NZ	2010			85,6	81,7	65,6	69,2	68,9	39,7	23,8	21,4	25,8	30,0	0,2	8,9	8,9	13,4	17,8
Riwaka	NZ	2012			73,8	44,4	32,5	24,9	26,3	34,7	10,2	10,7	10,4	13,6	1,8	4,3	5,3	10,5	14,0
Southern Cross	NZ	2010			149	140	119	112	118	48,5	15,9	13,3	13,8	16,8	0,4	6,8	6,3	8,4	12,3
Wai-iti	NZ	2012			68,8	42,7	31,6	24,8	24,7	38,8	5,5	5,1	5,1	5,7	2,0	3,2	3,4	6,6	8,1
Waimea	NZ	2012			71,2	50,4	37,9	29,8	33,3	70,4	10,1	8,0	8,2	9,9	2,5	6,2	5,4	10,7	14,3
Amarillo	US	2008	#1		191	156	122	115	120	64,3	55,8	56,0	62,3	73,0	0,2	8,8	12,7	24,1	31,7
Amarillo	US	2008	#2		224	196	159	141	147	77,4	76,5	68,1	71,1	76,6	0,2	16,8	20,1	42,6	51,3
Apollo	US	2008	#1		60,0	62,5	52,9	49,7	51,7	81,6	37,5	21,8	25,9	26,8	0,4	6,6	7,3	12,1	16,2
Apollo	US	2008	#2	50	74,0	82,3	59,4	59,4	51,3	75,3	34,1	17,7	23,9	41,1	0,4	16,3	11,5	18,6	20,8
Apollo	US	2010			27,7	26,1	18,9	16,3	17,4	23,7	10,0	3,9	3,8	4,4	0,1	5,1	3,4	4,0	5,0
Bravo	US	2008	#1		111	95,8	76,8	75,0	78,0	252	84,7	56,3	58,0	69,0	0,7	16,6	18,1	28,6	35,6
Bravo	US	2008	#2	48	104	99,0	74,6	77,5	79,4	269	107	57,8	69,0	76,0	2,3	41,6	29,9	39,1	47,8
Bravo	US	2010			34,6	32,9	25,2	21,5	22,7	70,1	26,8	10,7	9,8	11,0	0,2	13,7	9,8	10,8	12,5
Cascade	US	2007		46	73,7	47,6	44,0	42,3	43,8	164	25,6	16,1	20,3	18,9	0,1	10,3	11,0	17,2	21,3
Cascade	US	2008	#1	48	68,6	50,0	38,9	38,9	40,1	65,3	34,3	28,7	27,4	31,1	0,4	12,1	10,3	16,8	24,7
Cascade	US	2008	#2		63,7	53,9	39,2	37,0	35,7	137	30,1	15,4	21,3	22,1	0,2	14,9	11,2	27,5	29,2
Cascade	US	2008	#3		59,5	55,5	39,8	36,3	39,3	127	43,9	22,5	25,0	26,0	0,2	15,0	10,1	18,3	21,3
Chinook	US	2008			72,1	57,7	43,9	43,5	44,3	146	46,2	33,9	39,0	41,4	0,6	9,6	10,8	19,8	24,3
Citra	US	2007			97,4	70,3	58,0	51,6	56,4	119	21,5	10,0	10,6	10,1	0,2	8,6	7,4	11,5	15,2
Citra	US	2008	#1		195	160	114	108	108	87,5	25,6	15,1	20,8	22,6	0,5	12,3	11,1	24,4	27,4
Citra	US	2008	#2		139	131	102	102	92,4	66,9	23,5	17,0	23,6	25,7	0,7	13,3	11,7	21,0	24,6
Citra	US	2008	#3		57,0	48,1	37,8	33,6	33,2	33,0	9,7	5,5	5,2	5,8	0,3	5,9	5,2	5,5	7,3
Galcier	US	2008			83,8	81,1	55,6	52,1	49,6	13,0	6,7	3,8	5,2	5,9	0,7	3,0	2,4	6,7	7,8
HBC366	US	2012			19,3	19,1	18,6	19,4	19,6	9,4	5,7	6,2	7,8	9,1	0,2	5,0	8,5	9,6	36,3
Millenium	US	2007		46	49,6	38,4	31,1	29,8	30,9	24,5	8,4	5,0	6,0	5,2	0,1	3,1	3,0	4,6	5,5
Mosaic	US	2008	#1		110	98,2	71,3	68,4	70,1	171	56,4	33,1	38,7	47,0	0,6	13,6	11,1	21,4	27,8
Mosaic	US	2008	#2	48	84,2	95,4	76,3	74,1	78,0	151	73,7	60,1	44,8	55,2	0,7	29,2	19,7	24,5	31,9
Mosaic	US	2012			46,9	47,5	39,1	38,1	41,7	24,9	10,8	7,9	10,9	13,8	0,2	5,6	5,5	14,3	21,4
Mt.Hood	US	2008			148,7	126,4	88,8	80,4	78,6	54,2	17,7	7,9	11,1	12,2	0,5	8,3	5,6	15,0	16,3
Nugget	US	2007		46	126	89,6	70,8	70,9	71,6	9,2	4,0	3,3	3,2	3,3	0,1	1,6	1,3	2,6	3,0
Simcoe	US	2008	#1		41,2	36,9	27,2	25,1	27,0	38,0	14,1	9,1	10,1	10,9	0,2	3,4	3,4	5,9	8,9
Simcoe	US	2008	#2	50	38,8	34,6	25,7	28,3	24,8	28,1	10,7	7,7	10,0	15,8	0,3	6,2	6,6	9,9	14,4
Sorachi Ace	US	2009			138	125	91,6	86,9	90,7	127	35,3	18,7	19,1	17,3	0,5	19,1	11,3	16,9	18,6
Summit	US	2012			46,7	53,3	44,1	43,3	48,6	14,8	14,4	14,9	19,8	23,6	0,2	5,3	7,3	21,5	31,3

Table 2 **Comparison of Monoterpene Alcohols (nerol and α-terpineol) (µg/L) during Fermentation of Late-Hopped Beer: area, grown area; rp, repeating trial using same crop sample; ref, reference number (previously reported data); F., primary fermentation; 3d, 3 days; S., storage; 1w, 1 week**

					nerol (µg/L)					α-terpineol (µg/L)				
variety	**area**	**crop**	**rp**	**ref**	**wort**	**F. 3d**	**F. end**	**S. 1w**	**beer**	**wort**	**F. 3d**	**F. end**	**S. 1w**	**beer**
Saaz	CZ	2007			0,5	1,1	0,5	0,8	0,9	1,9	9,1	14,1	24,3	20,2
Hallertauer Tradition	GER	2007		46	1,4	0,4	0,3	0,4	0,6	5,4	4,7	3,7	3,7	3,9
Hallertauer Tradition	GER	2009	#1		0,9	1,3	0,8	0,8	0,9	2,6	6,2	15,7	18,4	19,9
Hallertauer Tradition	GER	2009	#2		1,0	0,9	0,9	1,2	2,0	3,1	8,6	17,0	14,1	13,9
Comet	GER	2014			0,5	0,4	0,8	1,0	1,1	1,9	0,8	0,6	0,2	0,2
Hallertau Blanc	GER	2012			0,6	0,9	0,9	1,3	1,9	2,0	2,5	3,0	3,1	5,1
Huell Melon	GER	2012			1,8	1,4	1,1	1,7	2,1	1,6	1,9	2,5	3,4	4,8
Mandarina Bavaria	GER	2012			2,6	1,5	1,0	1,4	2,0	2,1	2,6	2,4	2,9	4,2
Polaris	GER	2012			1,3	2,1	1,9	2,9	3,7	3,2	5,0	5,0	6,9	8,5
Aramis	FR	2013			0,6	0,4	0,5	0,5	1,5	3,0	1,7	1,6	1,1	1,8
Barbe Rouge	FR	2013			1,1	0,7	0,6	1,0	1,4	2,6	2,8	2,4	2,0	2,9
Mistral	FR	2015			0,9	0,6	0,6	0,4	0,7	1,4	0,5	0,3	0,2	0,2
Triskel	FR	2013			0,9	0,5	0,8	1,0	1,0	4,1	2,3	1,1	1,1	1,4
Furano Beauty	JP	2009			5,7	5,3	4,1	3,9	4,7	11,2	14,0	13,8	16,7	16,0
Furano No. 18	JP	2009			2,2	2,7	1,7	2,0	2,3	4,5	9,2	10,7	12,5	13,0
9702A	JP	2007		46	5,9	1,9	1,4	1,3	2,1	17,4	16,6	13,1	11,8	12,9
9803A	JP	2007		46	5,9	1,9	1,2	1,2	2,1	13,2	11,8	9,5	8,2	9,3
0612B	JP	2009			10,8	7,5	4,5	4,9	5,0	9,8	10,9	13,6	14,9	11,9
Galaxy	AUS	2013			0,7	1,1	1,8	2,2	4,5	2,8	2,8	2,1	2,0	2,6
Vic Secret	AUS	2014			0,3	2,7	4,3	5,4	12,2	2,6	2,1	1,4	0,4	0,1
Motueka	NZ	2010			3,2	2,7	2,5	2,7	2,8	2,7	26,9	35,7	38,2	24,1
Nelson Sauvin	NZ	2007			0,8	0,9	0,8	1,0	1,5	2,6	7,8	14,9	21,6	19,4
Pacific Jade	NZ	2010			1,1	1,5	1,5	1,7	2,6	2,5	25,4	34,8	36,0	23,0
Rakau	NZ	2012			1,9	0,8	0,7	0,8	0,7	2,3	1,4	14,9	10,8	18,9
Riwaka	NZ	2010			0,9	1,8	1,7	2,1	2,4	1,8	26,2	33,5	39,4	24,3
Riwaka	NZ	2012			1,6	0,8	0,8	0,9	1,4	2,0	1,2	14,7	11,3	19,2
Southern Cross	NZ	2010			1,4	1,5	1,7	1,8	2,1	3,0	24,9	35,9	38,9	27,0
Wai-iti	NZ	2012			2,0	0,9	0,7	0,8	1,0	2,0	1,5	14,4	10,3	19,8
Waimea	NZ	2012			2,3	1,0	0,8	0,9	1,5	2,3	1,5	14,9	11,2	20,6
Amarillo	US	2008	#1		1,6	3,2	3,6	4,6	5,4	0,8	1,6	3,0	3,5	1,9
Amarillo	US	2008	#2		2,6	5,6	5,9	6,6	7,1	4,1	8,2	9,7	8,8	8,1
Apollo	US	2008	#1		2,4	3,5	2,6	3,0	3,3	0,8	1,6	2,8	3,5	2,7
Apollo	US	2008	#2		3,8	6,4	3,9	5,0	6,9	5,7	7,5	6,7	17,7	17,0
Apollo	US	2010			1,6	1,7	1,0	1,0	1,1	7,9	7,5	6,2	6,3	6,7
Bravo	US	2008	#1		8,0	7,6	6,3	6,9	7,7	1,2	1,8	3,0	3,7	2,8
Bravo	US	2008	#2		13,2	14,6	10,2	12,6	14,3	1,2	2,0	1,3	1,4	1,7
Bravo	US	2010			3,5	2,9	1,7	1,6	2,0	8,8	8,7	7,6	6,3	6,4
Cascade	US	2007		46	1,5	1,5	1,1	1,3	2,1	7,1	5,0	4,0	3,8	2,7
Cascade	US	2008	#1		2,2	3,6	2,8	2,7	2,2	1,5	2,9	2,3	3,3	3,3
Cascade	US	2008	#2		1,5	2,5	1,7	2,6	2,7	4,2	9,4	15,2	23,6	21,4
Cascade	US	2008	#3		1,8	3,4	2,3	2,2	2,8	3,8	7,5	17,8	18,5	18,9
Chinook	US	2008			3,5	3,0	2,4	3,0	3,4	0,6	1,2	2,7	3,3	1,4
Citra	US	2007			2,7	1,8	1,2	1,2	1,4	7,5	6,4	4,9	4,1	3,2
Citra	US	2008	#1		4,5	3,7	2,2	3,0	3,3	5,3	9,9	17,2	25,1	21,9
Citra	US	2008	#2		4,4	4,3	3,1	3,7	4,1	4,6	5,9	7,9	16,1	13,7
Citra	US	2008	#3		3,1	2,3	1,5	1,4	1,9	5,6	5,4	4,9	4,1	4,7
Galcier	US	2008			0,8	1,2	0,6	1,2	1,3	2,2	8,7	14,1	23,7	20,4
HBC366	US	2012			0,5	3,5	6,1	5,0	28,3	2,7	2,3	1,9	1,5	1,8
Millenium	US	2007		46	1,4	1,2	0,8	0,8	0,9	6,6	5,9	4,4	4,2	3,1
Mosaic	US	2008	#1		7,5	6,0	4,2	5,2	5,6	0,9	1,8	3,2	3,7	2,2
Mosaic	US	2008	#2		10,8	11,9	9,6	9,3	11,1	0,7	2,1	1,2	1,3	1,6
Mosaic	US	2012			2,5	2,3	1,8	2,8	3,4	2,7	2,9	3,6	3,5	4,4
Mt.Hood	US	2008			1,2	2,4	1,3	2,3	2,4	3,6	9,9	15,3	23,4	21,8
Nugget	US	2007		46	1,1	1,0	0,6	0,8	0,8	8,9	7,0	5,0	4,6	3,4
Simcoe	US	2008	#1		1,5	2,1	1,7	1,7	2,1	0,5	1,1	2,3	3,0	1,5
Simcoe	US	2008	#2		1,8	2,8	2,0	2,7	3,1	3,0	8,1	17,1	12,1	13,0
Sorachi Ace	US	2009			5,3	5,4	3,3	3,5	3,7	12,3	16,3	14,2	17,0	22,9
Summit	US	2012			0,7	1,4	1,5	2,3	2,9	4,1	4,7	4,5	5,1	6,6

2.3 Standard products

Linalool (>98%, racemic mixture), α-terpineol (>95%, racemic mixture), nerol (>98%) and β-citronellol (>92%, racemic mixture) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Geraniol (98%) was purchased from Aldrich Chemical Company Inc.. Sumizyme BGA [β-1,4-glucosidase (EC 3.2.1.21), derived from *Aspergillus niger*, 2000 U/g (pH 4.0)] was obtained from Shin Nihon Chemical Co., Ltd. (Aichi, Japan).

2.4 Quantification of hop-derived monoterpene alcohols by solid phase microextraction-gas chromatography-mass spectroscopy (SPME-GC-MS)

For analysis of monoterpene alcohols (linalool, α-terpineol, nerol, β-citronellol, and geraniol), GC-MS analyses were carried out using a 6890N gas chromatograph (Agilent Technologies) and a MS 5973 mass spectrometer (Agilent Technologies) according to the method described in previous papers [46–48]. The carrier gas was helium, with a column-head pressure of 15 psi and flow rate of 1.8 mL/min. The detector was functioned in the EI mode (70 eV) and was connected to the GC by a transfer line heated to 280 °C. For analysis of wort, fermenting beer, and finished beer, 8 mL of each sample was put into a 20-mL glass vial including 3 g of sodium chloride at 0 °C. The vial, including a sample, was sealed with a magnet cap. The vial was preincubated with stirring at 40 °C for 15 min using a Combi-PAL autosampler (CTC Analytics). After preincubation, an SPME fiber [PDMS (polydimethylsiloxane), 100-µm film thickness; Supelco] was inserted into the head space of the vial and adsorption was carried out for 15 min. After the adsorption, the SPME fiber was injected into a splitless injector (260 °C; purge time = 3 min, purge flow = 20 mL/min) at oven temperature (50 °C) onto a type HP-1MS capillary column (30 m, 0.25-mm i.d., 1.0-µm film thickness; Agilent Technologies). For all the analyses, the temperature program was as follows: 50 °C for 1 min, raised at 5 °C/min to 250 °C, followed by a 1-min isotherm. The monoterpene alcohols (linalool, α-terpineol, nerol, β-citronellol, and geraniol) were quantified in the SIM mode, selecting the following ions: m/z 93 (for α-terpineol, nerol, and geraniol), and 109 (for linalool and β-citronellol). Calibration curves were determined using water (including 5% ethanol) containing these compounds at final concentrations ranging from 0 to 10 µg/L. All calibration produced a linear response with an R^2 value >0.98 over the concentration range analyzed. The analysis was performed in duplicate.

2.5 Estimation of glycosidically-bound monoterpene alcohol potential

In order to estimate the glycosidically-bound monoterpene alcohol potential of fermenting beer, an excess of the β-glucosidase Sumizyme BGA was added into beer for liberation of flavour compounds from their glycosidically-bound precursors. For removal of yeast, the beer sample was centrifuged at 5000 rpm for 10 min. An 8 mL sample of centrifuged beer was placed into a 20 mL glass vial, and 80 mg of Sumizyme BGA was added to this beer at 0 °C. For the blank, no Sumizyme BGA was added. This vial was sealed with a silicone rubber septum and an aluminium cap and was incubated at 50 °C for 60 min. After incubation, this vial was cooled on ice-water and was decapped. A 3 g portion of sodium chloride was added to the beer, and the vial was resealed with a magnet cap.

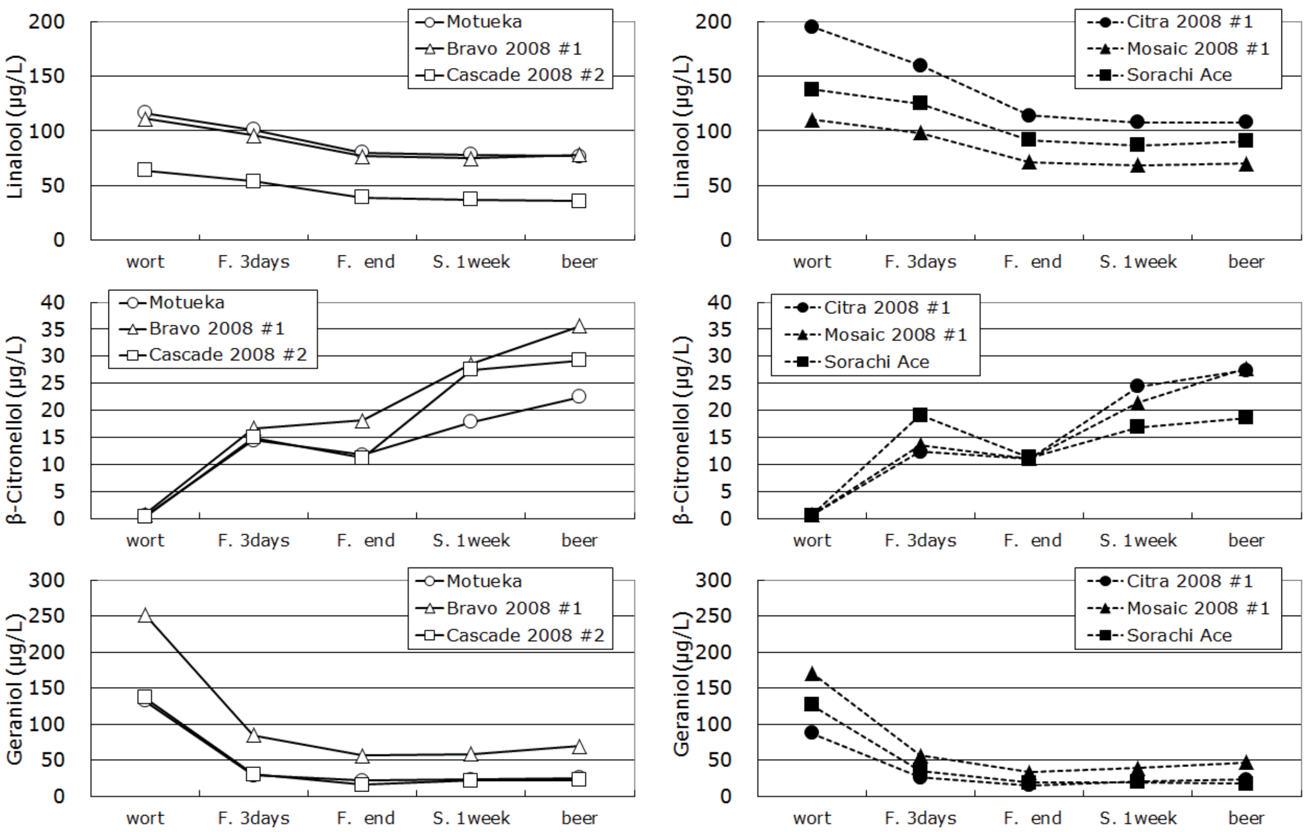

Fig. 2 Comparison of monoterpene alcohols (linalool, geraniol, and β-citronellol) (µg/L) during fermentation of beers late-hopped with Motueka, Bravo, Cascade, Citra, Mosaic, or Sorachi Ace: F., primary fermentation; S., srorage

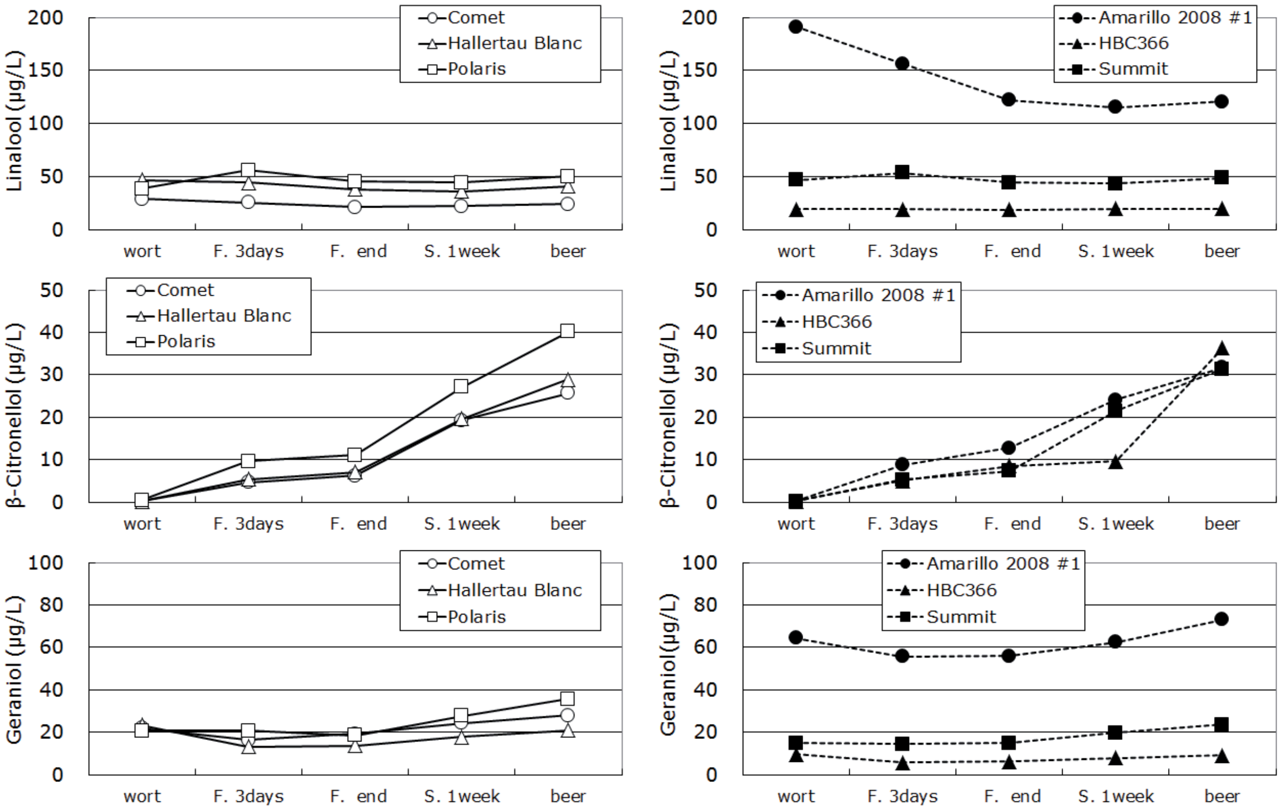

Fig. 3 **Comparison of monoterpene alcohols (linalool, geraniol, and β-citronellol) (µg/L) during fermentation of beers late-hopped with Comet, Hallertau Blanc, Polaris, Amarillo, HBC366, or Summit: F., primary fermentation; S., srorage**

Subsequently, the measurement of monoterpene alcohols was carried out by using GC-MS as described above. The liberation of each monoterpene alcohol was calculated by subtracting the concentration of each monoterpene alcohol in a blank from that in an enzyme-reacted sample. This liberation was regarded as the glycosidically-bound monoterpene alcohol potential.

3 Results and discussions

3.1 Comparison of behaviours of hop-derived monoterpene alcohols among total 42 hop varieties

In previous reports [46–48], certain geraniol-rich hop varieties have been mainly focused on and compared their behaviour of monoterpene alcohols during fermentation. In this study, we compared the behaviours of all monoterpene alcohols (linalool, geraniol, β-citronellol, nerol, and α-terpineol) among 42 hop varieties, including not only newly bred 'Flavour hops' but also traditional aroma hops and high alpha hops all around the world. All brewing trials were conducted with late-hopping using same flavouring hop dosage (0.8 g/L). All results are summarized in table 1 and 2.

In previous report, thresholds of linalool, geraniol, and β-citronellol were estimated at 3 µg/L, 7 µg/L and 9 µg/L, respectively (in model carbonated dilute alcohol solution (5 % v/v ethanol)) [46]. Table 1 shows that the linalool is most dominant component among all monoterpene alcohols, and that the geraniol is more variety-specific than linalool. The β-citronellol was almost absent in hop and wort and gently increased during total fermentation period. As well as reported in previous studies [46–48], the hop varieties originated in Europe (Saaz, Hallertauer Tradition, and Nugget) contained small amount of geraniol. On the other hand, most of the finished beers brewed with newly bred hop varieties contained not only linalool but also geraniol and β-citronellol at relatively high levels. In addition, it was also found that very unique behaviour of geraniol and β-citronellol in certain hop varieties. This finding is discussed in the next section.

The thresholds of nerol and α-terpineol were estimated at 80 µg/L and 450 µg/L, respectively (in model carbonated dilute alcohol solution (5 % v/v ethanol)) [46]. Table 2 clearly shows that the contents of nerol and α-terpineol in test-brewed beers made with various hops were at very small levels in comparison with their thresholds. In the viewpoint of sensory chemistry, it could be assumed that nerol and α-terpineol might have additive effects and/or synergy toward three other monoterpene alcohols (linalool, geraniol, and β-citronellol). These possibilities have not been sufficiently investigated yet. For example, synergy between nerol and β-caryophyllene has been proposed [12]. Monoterpene alcohols including nerol was regarded as important flavourants for varietal aroma of Sorachi Ace hop, because of synergy between these compounds and geranic acids [30, 51]. However, the result in table 2 suggested that contributions of nerol and α-terpineol to hopped beer flavour might be less important than those of linalool, geraniol, and β-citronellol.

3.2 Two different behaviours of hop-derived geraniol during fermentation

In general, the geraniol drastically decreases during first 3 days of fermentation. The β-citronellol was almost absent in hop and wort and gently increased during total fermentation period [46–48]. Most of geraniol-containing/geraniol-rich hop varieties in table 1 showed such behaviour of geraniol and β-citronellol. Typical behaviours of monoterpene alcohols using geraniol-rich hops, for example Motueka, Bravo, Cascade, Citra, Mosaic, and Sorachi Ace, were shown in figure 2.

However, several varieties, for example Comet, Hallertau Blanc, Polaris, Amarillo, HBC366, and Summit, showed very unique behaviours of geraniol and β-citronellol (Figure 3). The initial worts made with these varieties contained relatively small amount of geraniol (below 25 µg/L, except for Amarillo (approximately 60–80 µg/L in Table 1)). In the first 3 days of fermentation, the drastic decrease of geraniol was not observed and geraniol retained flat or slightly decreased. However, the β-citronellol gently increased up to 25–40 µg/L during total fermentation period, as well as observed in geraniol-rich hops (Figure 3). In such hops, geraniol precursors might be more dominant than free geraniol.

From these results, it was suggested that a group of geraniol-rich 'Flavour hop' varieties, which could generate a large amount of β-citronellol to finished beer, could be furthermore classified into two types, 'free geraniol dominant hops' and 'geraniol precursor dominant hops'.

Of all 42 varieties, most of geraniol-rich varieties were classified into 'free geraniol dominant hops'. Among such hops, 0612B, Motueka, Bravo, Cascade, Chinook, Citra, Mosaic, and Sorachi Ace contained especially large amount of free geraniol. On the other hand, only certain varieties, for example Vic Secret, Comet, Hallertau Blanc, Polaris, Amarillo, HBC366, and Summit were classified into'geraniol precursor dominant hops'.

3.3 Comparison of the glycosidically-bound flavour potentials in fermenting beers at storage 1 week

As described above, the occurrence of geranyl esters [7–8, 23, 26, 49] and glycosidically-bound geraniol precursors [2, 10, 16, 22, 25, 35-36, 46] has been proposed as possible geraniol precursors. In previous study, the evaluation of glycosidically-bound flavour potential in fermenting beer has been reported [46]. It is assumed that the flavour compounds could be released from glycosidically-bound precursors with an excess of β-1,4-glucosidase. Sumizyme BGA, which is a Japanese commercial enzyme used for flavour enhancement of wines and green teas, was used as the β-1,4-glucosidase. A release of monoterpene alcohols at 50 °C for 60 min were regarded as a flavour potential in a sample [46]. The fermenting beer after storage for 1 week were selected as a sample for evaluation of glycosidically bound flavour potential, because the increase of β-citronellol continued from storage for 1 week to the finished beer. A part of test-beers shown in table 1 was

Table 3 **Comparison of the glycosidically-bound flavour potentials in fermenting beers at storage 1 week: Glycosidically-bound flavor potential, liberation of each monoterpene alcohol by exogenous β-glucosidase (Sumizyme BGA); area, grown area; rp, repeating trial using same crop sample; ref, reference number (previously reported data); tr, trace.**

					linalool	geraniol	β-citronellol	nerol	α-terpineol
variety	area	crop	rp	ref	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
Saaz	CZ	2008			5,0	0,8	tr	0,3	9,0
Hallertauer Tradition	GER	2007		46	3,7	1,1	0,4	0,2	5,7
9702A	JP	2007		46	16,5	1,3	0,9	0,4	8,5
9803A	JP	2007		46	8,9	1,5	0,8	0,6	6,1
Nelson Sauvin	NZ	2007			5,6	1,7	0,1	0,3	12,7
Amarillo	US	2008	#1		17,0	21,1	4,3	2,5	tr
Apollo	US	2008	#1		4,9	8,4	1,7	1,2	tr
Bravo	US	2008	#1		4,1	20,0	1,4	3,2	tr
Cascade	US	2007		46	1,0	5,2	0,8	tr	1,8
Cascade	US	2008	#2		3,5	5,9	tr	0,5	8,8
Chinook	US	2008			6,0	13,2	1,0	2,1	tr
Citra	US	2007			tr	2,6	tr	tr	1,9
Citra	US	2008	#1		6,5	5,5	tr	1,3	9,4
Galcier	US	2008			11,9	2,8	0,2	1,2	9,7
Millenium	US	2007		46	0,2	1,2	tr	tr	1,4
Mosaic	US	2008	#1		3,9	14,4	1,2	2,3	1,7
Mt.Hood	US	2008			9,5	5,1	0,7	1,0	10,1
Nugget	US	2007		46	5,4	0,8	0,1	tr	1,2
Simcoe	US	2008	#1		3,1	3,0	tr	1,1	tr

applied for this analysis. As a result, there were flavour potentials of monoterpene alcohols in fermenting beers after storage for 1 week and these potentials varied depending on the hop cultivar (Table 3). Especially, the glycosidically-bound geraniol potentials in these samples were at up to 20 µg/L, which were enough for explaining the increase of β-citronellol during storage period. Amarillo, one of the 'geraniol precursor dominant hops', showed a maximum glycosidically-bound geraniol potential. A part of 'free geraniol dominant hops', Bravo, Chinook and Mosaic, also showed glycosidically-bound geraniol potential at relatively high levels.

In the viewpoint of geranyl esters, *Forster* et al. have reported that Hallertau Blanc and Polaris contained small amount of free geraniol and large amount of geranyl acetate in hops and the degradation of geranyl acetate to geraniol during fermentation was observed [7–8]. It is thought that released geraniol could be converted to β-citronellol during fermentation of beers made with these hops. From these results and previous studies, both of glycosidically-bound geraniol precursor and geranyl esters could function as a source of geraniol and β-citronellol during fermentation.

4. Conclusions

In this study, hop-derived monoterpene alcohols (linalool, geraniol, β-citronellol, nerol, and α-terpineol) and their behaviour during fermentation have been focused on. Total 42 hop varieties were compared. As a result, it was suggested that a group of geraniol-rich 'Flavour hop' varieties, which could generate a large amount of β-citronellol to finished beer, could be furthermore classified into two types, 'free geraniol dominant hops' and 'geraniol precursor dominant hops'. 'Free geraniol dominant hops' mainly contain free geraniol at high levels and subsidiary geraniol precursors. Most of 'geraniol-rich hops' was classified into this type, for example Motueka, Bravo, Cascade, Citra, Mosaic, Sorachi Ace, 0612B and so on. 'Geraniol precursor dominant hops' might mainly contain geraniol precursors at high levels and subsidiary free geraniol, for example, Vic Secret, Comet, Hallertau Blanc, Polaris, Amarillo, HBC366, and Summit. These results are useful for selecting hop variety tailored to the flavour of targeting beer styles.

It is thought that not only monoterpene alcohols but also various esters, for example isobutyric esters, esters of branched- chain fatty acids, and so on, could contribute to hopped beer flavour. Behaviours of such compounds during fermentation will be discussed in next paper.

Acknowledgment

We thank Yakima Chief, Inc., John I. Haas, Inc., Hop Breeding Company, LLC, S. S. Steiner, Inc., Joh Barth & Sohn GmbH & Co. KG, Comptoir Agricole, Hop Products Australia, and New Zealand Hops Ltd. for supplying hop samples; all panelists at Sapporo Breweries Ltd. for their sensory work; *Reika Miyamoto* at the Frontier Laboratories of Value Creation for technical assistance; and *Akira Inaba* and *Narushi Suda*, at the Bioresources Research & Development Department and *Toshiyuki Oshima* and *Takeshi Nakamura* at the Frontier Laboratories of Value Creation for their kind help.

5 References

1. Beatson, R. A.; Ansell, K. A. and Graham, L. T.: Breeding, development, and characteristics of the hop (*Humulus lupulus*) cultivar 'Nelson Sauvin', New Zealand Journal of Crop and Horticultural Science, **31** (2003), no. 4, pp. 303-309.
2. Biendl, M.; Kollmannsberger, H. and Nitz, S.: Occurrence of glycosidically bound flavour compounds in different hop products, Proc. EBC 29th Congr., (2003), pp. 252-258 (CD-ROM).
3. Daenen, L.; Saison, D.; Sterckx, F.; Delvaux, F. R.; Verachtert, H. and Derdelinckx, G.: Screening and evaluation of the glucoside hydrolase activity in Saccharomyces and Brettanomyces brewing yearsts, J. Applied Microbiology, **104** (2008), no. 2, pp. 478-488.
4. Dresel, M.; Van Opstaele, F.; Praet, T.; Jaskula-Goiris, B.; Van Holle, A.; Naudts, D.; De Keukeleire, D.; De Cooman, L. and Aerts, G.: Investigation of the impact of the hop variety and the hopping technology on the analytical volatile profile of single-hopped worts and beers, BrewingScience – Monatsschrift für Brauwissenschaft, **66** (2013), no. 11/12, pp. 162-175.
5. Dresel, M.; Praet, T.; Van Opstaele, F.; Van Holle, A.; Naudts, D.; De Keukeleire, D.; De Cooman, L. and Aerts, G.: Comparison of the analytical profiles of volatiles in single-hopped worts and beers as a function of the hop variety, BrewingScience – Monatsschrift für Brauwissenschaft, **68** (2015), no. 1/2, pp. 8-28.
6. Eyres, G. T.; Marriott, P. J.; Dufour, J. -P.: Comparison of odor-active compounds in the spicy fraction of hop (*Humulus lupulus* L.) essential oil from four different varieties, J. Agric. Food Chem. **55** (2007), no. 15, pp. 6252-6261.
7. Forster, A. and Gahr, A.: On the fate of certain hop substances during dry hopping, BrewingScience – Monatsschrift für Brauwissenschaft, **66** (2013), no. 7/8, pp. 93-103.
8. Forster, A.; Gahr, A. and Van Opstaele, F.: On the transfer rate of geraniol with dry hopping, BrewingScience – Monatsschr. Brauwiss., **67** (2014), no. 3/4, pp. 60-62.
9. Forster, A. and Gahr, A.: A comparison of the analytical and brewing characteristics of Cascade and Comet hop varieties as grown in Yakima (USA) and Hallertau (Germany), BrewingScience – Monatsschrift für Brauwissenschaft, **67** (2014), no. 11/12, pp. 137-148.
10. Goldstein H.; Ting, P. L.; Schulze, W. G.; Murakami, A. A.; Lusk, L. T. and Young, V. D.: Methods of making and using purified kettle hop flavorants, US 2003/0138546 A1 Jul. 24, 2003.
11. Graves, I. R.; Brier, M. B.; Chandra, G. S. and Alspach, P. A.: Kettle hop flavour from New Zealand hop (*Humulus lupulus* L.) cultivars, Proceedings of the 27th Convention of the Institute and Guild of Brewing, Asia Pacific Section, Adelaide, Australia, 17-22 March 2002 (CD-ROM).
12. Hanke, S.; Herrmann, M.; Back, W.; Becker, T. and Krottenthaler, M.: Synergistic and suppression effects of flavour compounds in beer, Proc. 32nd EBC Congr., (2009), Lecture 21.
13. Hao, J.; Dong, J.; Yin, H.; Yan, P.; Ting, P. L.; Li, Q.; Tao, X.; Yu, J.; Chen, H. and Li., M.: Optimum method of analyzing hop derived aroma compounds in beer by Headspace Solid-Phase Microextraction (SPME) with GC/MS and their evolutions during Chinese lager brewing process, J. Am. Soc. Brew. Chem., **72** (2014), no. 4, pp. 261-270.
14. Hieronymus, S.: A taste for hops – Exploring the history and mystery of Flavor Hops, All About Beer Magazine, **34** (2013). (http://allaboutbeer.com/article/flavor-hops/)
15. Inui, T.; Tsuchiya, F.; Ishimaru, M.; Oka, K. and Komura, H.: Different beers with different hops. Relevant compounds for their aroma characteristics, J. Agric. Food Chem., **61** (2013), no. 20, pp. 4758-4764.

16. Kankolongo Cibaka, M.-L.; Ferreira, C. S.; Decourrière, L.; Lorenzo-Alonso, C.-J.; Bodart, E. and Collin, S.: Dry hopping with the dual-purpose varieties Amarillo, Citra, Hallertau Blanc, Mosaic, and Sorachi Ace.: Minor contribution of hop terpenol glucoside to beer flavor, J. Am. Soc. Brew. Chem., **75** (2017), pp. 122–129.
17. King, A. and Dickinson, J. R.: Biotransformation of monoterpene alcohols by *Saccharomyces cerevisiae*, *Torulaspora delbrueckii* and *Kluyveromyces lactis*, Yeast, **16** (2000), no. 6, pp. 499-506.
18. King, A. and Dickinson, J. R.: Biotransformation of hop aroma terpenoids by ale and lager yeasts, FEMS Yeast Research, **3** (2003), no. 1, pp. 53-62.
19. Kishimoto, T.; Wanikawa, A.; Kagami, N. and Kawatsura, K.: Analysis of hop-derived terpenoids in beer and evaluation of their behavior using the stir bar-sorptive extraction method with GC-MS, J. Agric. Food Chem. **53** (2005), no. 12, pp. 4701-4707.
20. Kishimoto, T.; Wanikawa, A.; Kono, K. and Shibata, K.: Comparison of the odor-active compounds in unhopped beer and beers hopped with different hop varieties, J. Agric. Food Chem., **54** (2006), no. 23, pp. 8855-8861.
21. Kishimoto, T.; Wanikawa, A.; Kono, K. and Aoki, K.: Odorants comprising hop aroma of beer: hop-derived odorants increased in the beer hopped with aged hops, Proc. 31st EBC Congr., (2007), pp. 226-235 (CD-ROM).
22. Kollmannsberger, H.; Biendl, M. and Nitz, S. Occurrence of glycosidically bound flavour compounds in hops, hop products and beer, Monatsschrift für Brauwissenschaft, **59** (2006), no. 5/6, pp. 83-89.
23. Lam, K. C.; Foster II, R. T. and Deinzer, M. L.: Aging of hops and their contribution to beer flavor, J. Agric. Food Chem., **34** (1986), no. 4, pp. 763-770.
24. Lutz, A.; Kammhuber, K. and Seigner, E.: New trend in hop breeding at the Hop Research Center Huell, BrewingScience – Monatsschrift für Brauwissenschaft, **65** (2012), no. 3/4, pp. 24-32.
25. Murakami, A. A., Navarro, A., Ryder, D. S. and Goldstein H.: Use of glycosides extracted from hop plant parts to flavor malt beverages, US 2003/0211788 A1 Nov. 13, 2003.
26. Peacock, V. E.; Deinzer, M. L.; Likens, S. T.; Nickerson, G. B. and McGill, L. A.: Floral hop aroma in beer, J. Agric. Food Chem., **29** (1981), no. 6, pp. 1265-1269.
27. Probasco, G.; Perrault J. and Varnum, S.: Citra – a new special aroma hop variety, World Brewing Congress 2008 Proceedings, Honolulu, Hawaii, 2008, Poster 115 (CD-ROM).
28. Probasco, G.; Varnum, S.; Perrault J. and Hysert, D.: Citra – a new special aroma hop variety, MBAA Tech. Quart., **47** (2010), no. 1, pp. 17-22.
29. Probasco, G.; Perrault J. and Varnum, S.: Mosaic HBC 369 – a new flavor hop variety, World Brewing Congress 2012 Proceedings, Portland, Oregon, 2012, Poster 147.
30. Sanekata, A.; Tanigawa, A.; Takoi, K.; Itoga, Y.; Sano, T.; Matsumoto, I.; Kaneko, T.; Nakayama, Y. and Tsuchiya Y.: The varietal aroma of 'Sorachi Ace' : Identification and characterization of the unique flavor compounds, World Brewing Congress 2016 Proceedings, Denver, Colorado, 2016, Lecture 49.
31. Schmidt, C. and Biendel, M.: Headspace Trap GC-MS analysis of hop aroma compounds in beer, BrewingScience – Monatsschrift für Brauwissenschaft, **69** (2016), no. 1/2, pp. 9-15.
32. Schönberger, C.: Unnachahmliche Noten. Flavour Hops – Herausstellungsmerkmal Hopfen, Brauindustrie, **97** (2012), no. 1, pp. 28-30.
33. Seaton, J. C.; Moir, M. and Sugget, A.: The refinement of hop flavour by yeast action, Proceedings of the 17th Convention of the Institute of Brewing, Australia and New Zealand Section, Perth, Australia, (1982), pp. 117-124.
34. Sharp, D. C.; Shaun Townsend, M.; Qian, Y. and Shellhammer, T. H.: Effect of harvest maturity on the chemical composition of Cascade and Willamette hops, J. Am. Soc. Brew. Chem., **72** (2014), no. 4, pp. 231-238.
35. Sharp, D. C.; Steensels, J. and Shellhammer, T. H.: The effect of hopping regime, cultivar and β-glucosidase activity on monoterpene alcohol concentrations in wort and beer, J. Inst. Brew., **123** (2017), no. 2, pp. 185-191.
36. Sharp, D. C.; Vollmer, D. M.; Qian, Y. and Shellhammer, T. H.: Examination of glycoside hydrolysis methods for the determination of terpenyl glycoside contents of different hop cultivars, J. Am. Soc. Brew. Chem., **75** (2017), no. 2, pp. 101-108.
37. Steinhaus, M.; Wilhelm, W. and Schieberle, P.: Comparison of the most odor-active volatiles in different hop varieties by application of a comparative aroma extract dilution analysis, Eur. Food. Res. Technol., **226** (2007), no. 1/2, pp. 45-55.
38. Steinhaus, M. and Schieberle, P.: Transfer of the potent hop odorants linalool, geraniol and 4-methyl-4-sulfanyl-2-pentanone from hops into beer, Proc. 31st EBC Congr., (2007), pp. 1004-1011 (CD-ROM).
39. Steyer, D.; Erny, C.; Claudel, P.; Riveill, G.; Karst, F. and Legras, J. -L.: Genetic analysis of geraniol metabolism during fermentation, Food Microbiol., **33** (2013), no. 2, pp. 228-234.
40. Steyer, D.; Clayeux, C. and Laugel, B.: Characterization of the terpenoids composition of beers made with the French hop varieties: Strisselspalt, Aramis, Triskel and Bouclier, BrewingScience – Monatsschrift für Brauwissenschaft, **66** (2013), no. 11/12, pp. 192-197.
41. Steyer, D. and Clayeux C.: Genetic metabolism of hop terpenoid compounds by yeast in beer, 35th EBC Congr., (2015), Lecture 20.
42. Suzuki, K.; Yabe, T.; Maruyama, Y.; Abe, K. and Nakajima, T.: Characterization of recombinant yeast exo-β-1,3-glucanase (Exg 1p) expressed in Escherichia coli cells, Biosci. Biotechnol. Biochem., **65** (2001), no. 6, pp. 1310-1314.
43. Takoi, K.; Tominaga, T.; Degueil, M.; Sakata, D.; Kurihara, T.; Shinkaruk, S.; Nakamura, T.; Maeda, K.; Akiyama, H.; Watari, J.; Bennetau, B. and Dubourdieu, D.: Identification of novel unique flavor compounds derived from Nelson Sauvin hop and development of new product using this hop, Proc. 31st EBC Congr., (2007), pp. 241-251 (CD-ROM).
44. Takoi, K.; Degueil, M.; Shinkaruk, S.; Thibon, C.; Maeda, K.; Ito, K.; Bennetau, B.; Dubourdieu, D. and Tominaga, T.: Identification and characteristics of new volatile thiols derived from the hop (*Humulus lupulus* L.) cultivar Nelson Sauvin, J. Agric. Food Chem., **57** (2009), no. 6, pp. 2493-2502.
45. Takoi, K.; Degueil, M.; Shinkaruk, S.; Thibon, C.; Kurihara, T.; Toyoshima, K.; Ito, K.; Bennetau, B.; Dubourdieu, D. and Tominaga, T.: Specific flavor compounds derived from Nelson Sauvin hop and synergy of these compounds, BrewingScience – Monatsschrift für Brauwissenschaft, **62** (2009), no. 7/8, pp. 108-118.
46. Takoi, K.; Koie, K.; Itoga, Y.; Katayama, K.; Shimase, M.; Nakayama, Y. and Watari, J.: Biotransformation of hop-derived monoterpene alcohols by lager yeast and their contribution to the flavor of hopped beer, J. Agric. Food Chem., **58** (2010), no. 8, pp. 5050-5058.
47. Takoi, K.; Itoga, Y.; Koie, K.; Kosugi, T.; Shimase, M.; Katayama, K.; Nakayama, Y. and Watari, J.: Contribution of geraniol metabolism to citrus flavour of beer: Synergy of geraniol and β-citronellol under coexistence with excess linalool, J. Inst. Brew., **116** (2010), no. 3, pp. 251-260.
48. Takoi, K.; Itoga, Y.; Takayanagi, J.; Kosugi, T.; Shioi, T.; Nakamura, T.

and Watari, J.: Screening of geraniol-rich flavor hop and interesting behavior of β-citronellol during fermentation under various hop-addition timings, J. Am. Soc. Brew. Chem., **72** (2014), no. 1, pp. 22-29.

49. Takoi, K.; Tokita, K.; Sanekata, A.; Usami, Y.; Itoga, Y.; Koie, K.; Matsumoto, I. and Nakayama, Y.: Varietal difference of hop-derived flavour compounds in late-hopped/dry-hopped beers, BrewingScience – Monatsschrift für Brauwissenschaft, **69** (2016), no. 1/2, pp. 1-7.
50. Takoi, K.; Itoga, Y.; Takayanagi, J.; Matsumoto, I. and Nakayama, Y.: Control of hop aroma impression of beer with blend-hopping using geraniol-rich hop and new hypothesis of synergy among hop-derived flavour compounds, BrewingScience – Monatsschrift für Brauwissenschaft, **69** (2016), no. 11/12, pp. 85-93.
51. Tanigawa, A.; Sanekata, A.; Takoi, K.; Takazumi, K.; Matsumoto, I. and Nakayama, Y.: Identification of geranic acid contributing to varietal aroma in Sorachi Ace and synergy with other hop-derived flavour compounds, 36th EBC Congr., (2017), Poster 60.
52. Vaudano, E.; Moruno, E. G. and Stefano, R. D.: Modulation of geraniol metabolism during alcohol fermentation, J. Inst. Brew., **110** (2004), no. 3, pp. 213-219.
53. Yuan, T. -T.; Chen, Q. -Q.; Pei-Ji Zhao, P. -J.; Zeng, Y.; Liu, X. -Z. and Lu, S.: Identification of enzymes responsible for the reduction of geraniol to citronellol, Nat. Prod. Bioprospect., **1** (2011), no. 3, pp. 108-111.

Received 29 August 2017, accepted 12 November 2017

View publication stats