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# Varietal Difference of Hop-Derived Flavour Compounds in Late-Hopped/Dry-Hopped Beers

Monoterpene alcohols (linalool,  $\beta$ -citronellol, nerol and geraniol) and their derivatives (geranyl acetate and *cis*-linalool oxide),  $\beta$ -ionone and several esters (isobutyl isobutyrate, isoamyl isobutyrate, 2-methylbutyl isobutyrate and ethyl heptanoate) were focused on as possible contributors on hop varietal aroma. We measured flavour compounds in late-hopped beers and dry-hopped beers brewed with eighteen hop varieties. On the basis of the results, we discuss the comparison of varietal profiles of hop-derived flavour compounds among eighteen hop varieties, the relationship among certain monoterpene alcohols and their derivatives and the effect of hopping procedure on the flavour profiles in beers.

As a result, the concentration profiles composed of linalool,  $\beta$ -citronellol, geraniol, geranyl acetate, *cis*-linalool oxide, isobutyl isobutyrate, isoamyl isobutyrate, 2-methylbutyl isobutyrate and ethyl heptanoate were widely variable among finished beers brewed with these eighteen hop varieties. However, nerol and  $\beta$ -ionone might not almost contribute to the hop varietal difference.

Descriptors: Beer, hop, varietal aroma, flavour compounds, terpenoids, esters

## 1 Introduction

It is well-known that hops contain various flavour compounds, for example terpene hydrocarbons, terpene alcohols, esters, ketones, short-chain fatty acids, sulfur compounds, and so on [1, 2]. In wort boiling process, these compounds are exposed under strong evaporation and heavy oxidative conditions. Subsequently, flavour compounds are affected by yeast fermentation, for example adsorption to foam and/or yeast cells, reduction, hydrolysis, esterification, biotransformation, and so on. Hop-derived flavour compounds in finished beer are survived or generated through such complicated brewing process [3–6].

In this paper, we focused on monoterpene alcohols (linalool,  $\beta$ -citronellol, nerol and geraniol) and their derivatives (geranyl acetate and linalool oxide),  $\beta$ -ionone and several esters (isobutyl isobutyrate, isoamyl isobutyrate, 2-methylbutyl isobutyrate and ethyl heptanoate) among many flavour compounds derived from hops (Figure 1).

Monoterpene alcohols, derived from hops, have been reported by many researchers [3, 4, 7–16]. Of all monoterpene alcohols, linalool is well known as a useful indicator of hopped beer flavour.  $\beta$ -Citronellol and geraniol are also important contributors to the

lime-like flavour of hopped beer. In our previous studies [3, 4, 6], the  $\beta$ -citronellol was almost absent in hop and wort and gently increased during fermentation, because of the biotransformation from geraniol to  $\beta$ -citronellol by brewing yeast. Though, in general, the geraniol drastically decreases during the first 3–4 days of fermentation, the concentration of geraniol and  $\beta$ -citronellol in beer

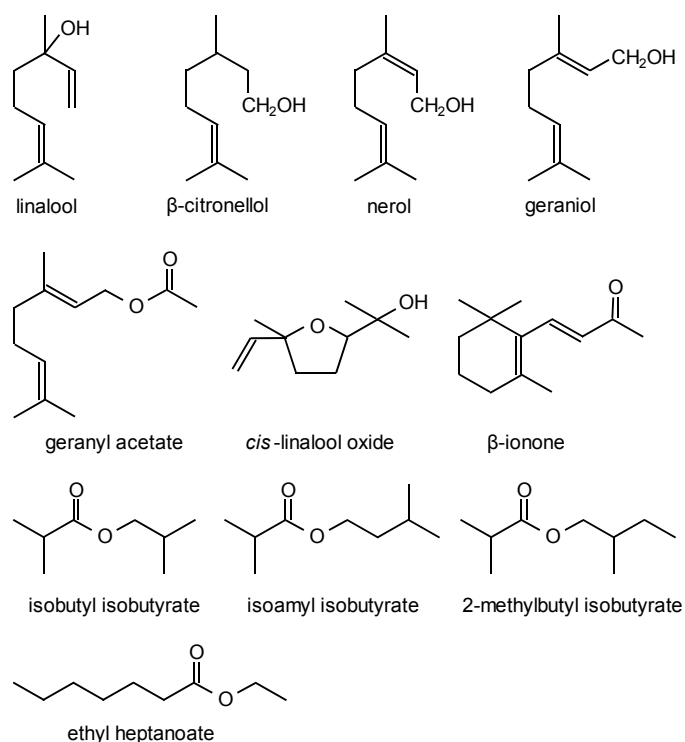


Fig. 1 Various flavour compounds derived from hops

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could be enriched depending on the initial geraniol content in the wort; for example, by using geraniol-rich hops. In addition, there was an additive effect among linalool, geraniol, and  $\beta$ -citronellol. In this case, linalool functioned as a flavour enhancer, and the flavour intensities of geraniol and  $\beta$ -citronellol could be enhanced when linalool was also present [3]. The flavor impression became lime-like by coexistence of these three monoterpene alcohols [4].

Geranyl acetate containing in hops and beers has been reported in several literatures [8, 9, 15, 17]. Lam et al. have proposed that geranyl acetate could be hydrolysed to geraniol during fermentation [8]. In recent years, Forster et al. reported that the beers dry-hopped with geranyl acetate-rich hops (Cascade, Hallertau Blanc and Polaris) contained a small amount of this compound and a large amount of geraniol [17]. This result strongly supports Lam's hypothesis.

It has been thought that linalool oxide could be derived by oxidation of linalool during wort boiling process [9, 18]. Haley et al. have compared various flavour compounds in late-hopped beer and dry-hopped beer and reported that both of *trans*- and *cis*-linalool oxide detected in late-hopped beer, not in dry-hopped beer [18].

$\beta$ -Ionone, which has a violet-like floral flavour, have detected in hops and beers. [9, 11, 12, 19]. Haley et al. have reported that  $\beta$ -ionone was not almost detected in late-hopped and dry-hopped beers by using Styrian Golding hop extract [18]. On the other hand, Kishimoto et al. reported an occurrence of  $\beta$ -ionone in late-hopped beers brewed with Saazer, Hersbrucker and Cascade hops [11] and dry-hopped beers with a bitter variety [12].

Isobutyric esters, including isobutyl isobutyrate, isoamyl isobutyrate and 2-methylbutyl isobutyrate, were widely found in various hops [18, 20–24]. These esters have a green apple, apricot-like flavour [23, 24]. Traditional bitter hops and modern high alpha hops, for example Northern Brewer, Nugget, Magnum, contain relatively high amount of these compounds. When looking at traditional aroma hops, German aroma hops, for example Hallertauer Tradition, contained these compounds while Saaz and Lublin had few of these compounds [22–24]. Seaton et al. reported that isobutyric esters could be unstable during boiling and fermentation [25]. In fact, commercial beers brewed with kettle hopping contain only small amounts of these compounds [23]. On the other hand, these compounds are found in late-hopped beer and dry-hopped beer [25–27]. Isobutyric esters are expected to contribute to some of the special flavours of dry-hopped beers.

Ethyl heptanoate could be formed from methyl heptanoate derived from hops [18]. Several researchers have reported an occurrence of methyl heptanoate in raw hop [20, 21]. Heptanoic acid is a minor metabolite induced during yeast fermentation. Therefore, methyl heptanoate in hop might behave as a precursor of ethyl heptanoate.

In this study, we analyse monoterpene alcohols (linalool,  $\beta$ -citronellol, nerol and geraniol) and their derivatives (geranyl acetate and linalool oxide),  $\beta$ -ionone and various esters (isobutyl isobutyrate, isoamyl isobutyrate, 2-methylbutyl isobutyrate and ethyl heptanoate), and compared varietal difference of hop-derived

flavour compounds in beers made with the U.S. hops, German hops and New Zealand hops.

## 2 Materials and methods

### 2.1 Hop raw materials

Apollo and Bravo were harvested in the U.S. in 2010. Citra was bred and grown in the U.S. in 2008. Mosaic and Summit were harvested in the U.S. in 2012. Hallertau Blanc, Hüll Melon, Mandarina Bavaria and Polaris were bred and grown in Germany in 2012. Hallertau Tradition (HHT) was harvested in Germany in 2011–2013. Motueka, Pacific Jade, Riwaka and Southern Cross were harvested in New Zealand in 2010. Kohatu, Nelson Sauvin, Rakau, Wai-iti and Wimea were harvested in New Zealand in 2012. All hops were used in form of pellet type 90.

### 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 a 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 5 min. 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  $15.0 \times 10^6$  cells/ml lager yeast (brewery collected; *Saccharomyces pastorianus*) to the wort. The temperature of the fermentation was maintained at 10–12°C (primary fermentation). For dry-hopping, the fermentation was started without addition of hop-flavoured wort and 24.8 g of hop was added to each fermentation tank in the third day (dry 1) or the sixth day (dry 2) of primary fermentation period, respectively. After transferring the fermented wort to another storage tank under a CO<sub>2</sub> 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.

### 2.3 Standard products

Linalool (> 98 %, racemic mixture), nerol (> 98 %) and  $\beta$ -citronellol (> 92 %, racemic mixture), linalool oxide (> 97 %, mixture of isomers) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Geraniol (98 %) was purchased from Aldrich Chemical Company Inc.. Isobutyl isobutyrate (> 98 %), isoamyl isobutyrate (> 98 %), isobutyric acid (> 98 %), 2-methylbutan-1-ol (> 97 %), ethyl heptanoate (> 97 %), geranyl acetate (> 95 %, mixture of isomers),  $\beta$ -ionone (> 95 %) and benzyl acetate (> 98 %) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). 2-Methylbutyl isobutyrate (> 97 %) was synthesized by esterification of isobutyric acid and 2-methylbutan-1-ol, as previously described [23–24]. As a result of our analysis, linalool oxide

contained *cis*-linalool oxide and *trans*-linalool oxide and the ratio of *cis*-linalool oxide was calculated as 0.563.

## 2.4 Quantification of hop-derived flavor compounds by solid phase microextraction-gas chromatography-mass spectroscopy (SPME-GC-MS)

For analysis of isobutyl isobutyrate, *cis*-linalool oxide, ethyl heptanoate, linalool, nerol,  $\beta$ -citronellol, geranyl acetate,  $\beta$ -ionone, GC-MS analyses were carried out using a 7890N gas chromatograph (Agilent Technologies, Palo Alto, CA). The carrier gas was helium with a column-head pressure of 6.5 psi and flow rate of 1.0 mL/min. The detector was a mass spectrometer (MS 5975, Agilent Technologies) functioning in the EI mode (70 eV) and was connected to the GC by a transfer line heated to 250 °C. An 8 mL sample of each beer was put into a 20 mL glass vial including 3 g of sodium chloride at 0 °C, together with 80  $\mu$ L of benzyl acetate solution (100 mg/L) as an internal standard (ISTD), and the vial 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, Zwingen, Switzerland). After preincubation, an SPME fibre [PDMS/DVB (polydimethylsiloxane/Divinylbenzene), 65  $\mu$ m film thickness, Supelco, Bellefonte, PA, USA] was inserted into the head space of the vial and adsorption was carried out for 15 min. After the adsorption, the SPME fibre was injected into a split injector (250 °C; split rate, 2:1; purge flow, 3 ml/min) at oven temperature (40 °C) onto a type DB-5MS capillary column [Agilent Technologies, 30 m, 0.25 mm internal diameter (i.d.), 0.25  $\mu$ m film

thickness]. For all the analyses, the temperature program was as follows: 40 °C for 5 min, raised at 5 °C/min to 90 °C, raised at 2 °C/min to 120 °C, raised at 5 °C/min to 150 °C, raised at 20 °C/min to 320 °C, followed by a 3 min isotherm. The flavour compounds, isobutyl isobutyrate, *cis*-linalool oxide, ethyl heptanoate, linalool, nerol,  $\beta$ -citronellol, geranyl acetate,  $\beta$ -ionone and benzyl acetate (ISTD) were quantified in the SIM mode, selecting the ions: *m/z* 71 and 43 for isobutyl isobutyrate, *m/z* 59 and 94 for *cis*-linalool oxide, *m/z* 88 and 113 for ethyl heptanoate, *m/z* 71 and 93 for linalool, *m/z* 84 and 93 for nerol, *m/z* 81 and 95 for  $\beta$ -citronellol, *m/z* 69 and 93 for geranyl acetate, *m/z* 177 and 43 for  $\beta$ -ionone and *m/z* 108 and 91 for benzyl acetate. Calibration curves were determined using test-beers containing these flavour compounds. Calibration curves of all eight compounds produced a linear response with an  $R^2$  value > 0.98 (Figure 2).

For analysis of isoamyl isobutyrate, 2-methylbutyl isobutyrate and geraniol, GC-MS analyses were carried out using a 6890N gas chromatograph (Agilent Technologies), a MS 5973 detector (Agilent Technologies), a type HP-1MS capillary column (30 m, 0.25 mm i.d., 1.0  $\mu$ m film thickness) (Agilent Technologies) and an SPME fibre (polydimethylsiloxane, 100  $\mu$ m film thickness; Supelco) according to the method described in previous papers [3, 4, 6]. Calibration curves were determined using water (including 5 % ethanol) containing these compounds at final concentrations ranging from 0 to 10  $\mu$ g/L or 0 to 1.0  $\mu$ g/L. All calibration produced a linear response with an  $R^2$  value > 0.98 over the concentration range analysed (Figure 2). The analysis was performed in duplicate.

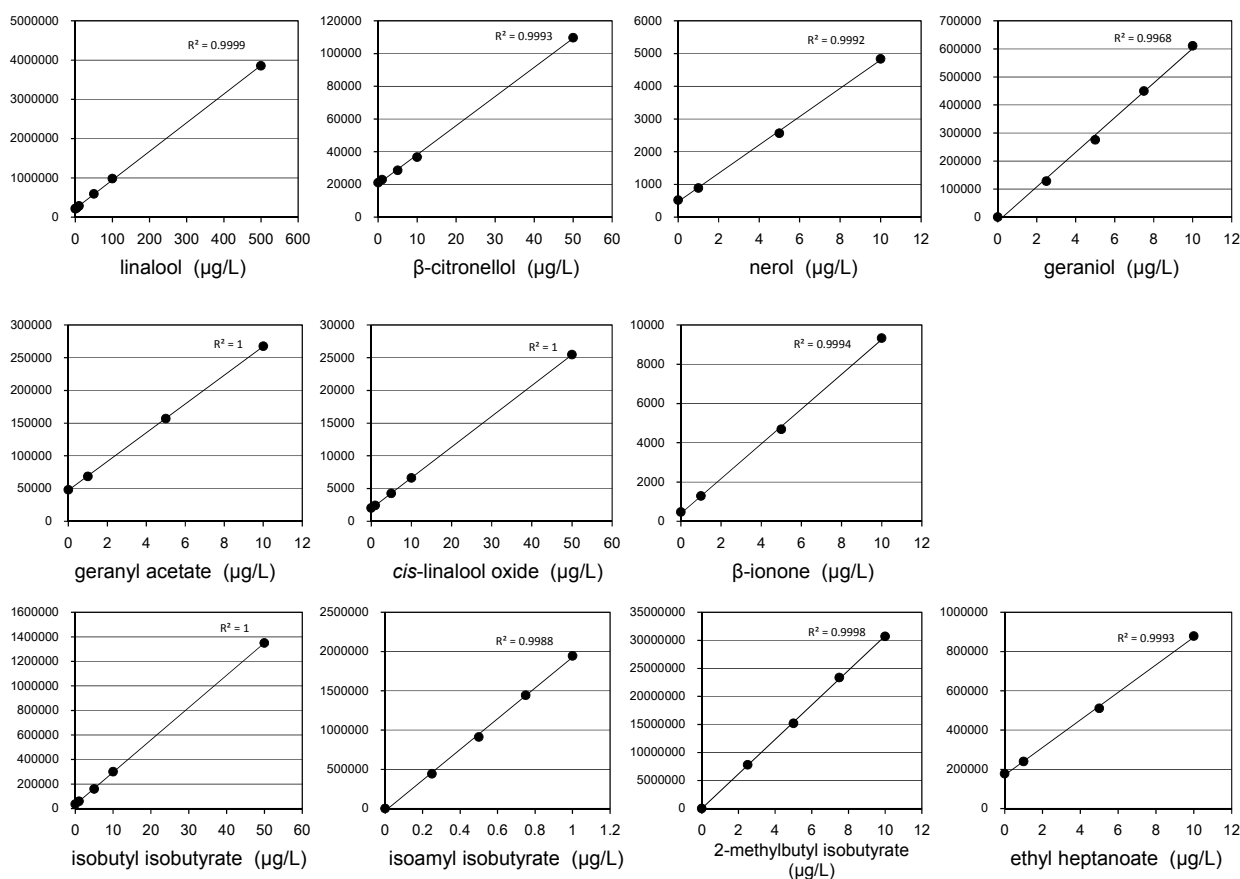


Fig. 2 Calibration curves obtained from two SPME-GC-MS methods

**Table 1** Compositions of hop-derived flavour compounds in test-brewed beers made with the U.S. hops and German hops

hop variety		Apollo	Bravo	Citra	Mosaic	Summit	Hallertau Blanc	Hüll Melon	Mandarina Bavaria	Polaris
crop		2010	2010	2008	2012	2012	2012	2012	2012	2012
flavouring hop (g/L of wort)		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
linalool	(µg/L)	27.8	34.0	52.9	50.9	60.2	51.3	28.1	42.1	62.6
β-citronellol	(µg/L)	11.8	31.9	17.3	24.3	34.5	32.1	15.0	17.8	43.8
nerol	(µg/L)	1.2	2.8	2.4	5.1	4.0	2.6	2.9	3.1	5.4
geraniol	(µg/L)	4.4	11.0	5.8	13.8	23.6	21.0	8.7	9.6	35.5
geranyl acetate	(µg/L)	2.2	2.9	1.6	2.0	3.7	2.5	1.0	1.4	5.8
cis-linalool oxide	(µg/L)	2.5	2.4	6.2	1.3	5.9	2.0	5.0	1.7	1.4
β-ionone	(µg/L)	0.1	0.1	0.1	tr	tr	0.1	0.1	0.1	tr
isobutyl isobutyrate	(µg/L)	1.4	1.3	0.9	10.1	2.8	10.0	25.2	22.4	54.0
isoamyl isobutyrate	(µg/L)	1.5	1.9	0.4	10.8	3.1	5.9	7.3	3.4	16.5
2-methylbutyl isobutyrate	(µg/L)	9.6	10.3	1.6	26.0	7.3	18.9	41.4	27.6	63.6
ethyl heptanoate	(µg/L)	2.5	2.8	2.6	5.7	2.6	2.7	3.1	4.4	8.8

**Table 2** Compositions of hop-derived flavour compounds in test-brewed beers made with New Zealand hops

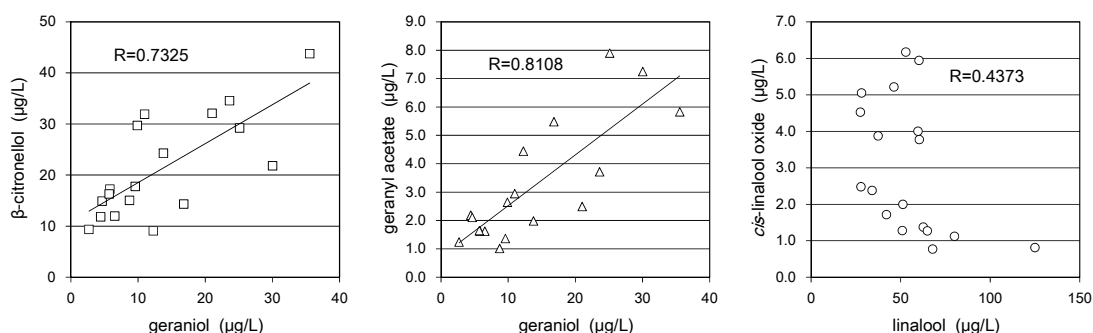
hop variety		Kohatu	Motueka	Nelson Sauvín	Pacific Jade	Rakau	Riwaka	Southern Cross	Wai-iti	Wimea
crop		2012	2010	2012	2010	2012	2010	2010	2012	2012
flavouring hop (g/L of wort)		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
linalool	(µg/L)	37.4	80.0	27.5	64.9	60.4	67.8	125.0	46.3	59.7
β-citronellol	(µg/L)	9.4	29.2	12.0	9.1	14.9	21.8	14.3	16.3	29.7
nerol	(µg/L)	1.6	2.0	2.6	1.1	2.1	1.5	1.2	2.2	2.4
geraniol	(µg/L)	2.7	25.1	6.5	12.3	4.7	30.0	16.8	5.7	9.9
geranyl acetate	(µg/L)	1.2	7.9	1.6	4.4	2.1	7.2	5.5	1.6	2.6
cis-linalool oxide	(µg/L)	3.9	1.1	4.5	1.3	3.8	0.8	0.8	5.2	4.0
β-ionone	(µg/L)	0.1	0.1	0.1	0.1	tr	0.1	tr	0.1	tr
isobutyl isobutyrate	(µg/L)	2.7	4.4	9.3	18.5	17.4	9.3	17.9	6.1	21.1
isoamyl isobutyrate	(µg/L)	0.6	1.2	1.6	3.1	1.8	4.0	5.3	1.4	1.7
2-methylbutyl isobutyrate	(µg/L)	3.3	18.1	17.8	78.1	26.3	38.6	103.6	16.4	35.2
ethyl heptanoate	(µg/L)	2.4	1.8	3.0	3.9	3.7	1.6	3.5	3.7	3.5

### 3 Results and discussions

#### 3.1 Varietal difference of hop-derived flavour compounds

In recent years, craft brewers have been brewing unique beers, made with characteristic hops, all around the world. These hops

could give citrus and/or exotic fruit-like flavours to finished beer. A group of such characteristic hops are often called “flavour hop” [28]. A beer brewed with such a flavour hop has very unique “varietal aroma.” Several researchers have tried to reveal variety-specific flavour compounds contributing to the varietal aroma derived from certain hops [3–4, 6–8, 11, 13–17, 23–24, 29–31]. However, possible contributors on the varietal aroma of each flavour hop have not been fully investigated yet.



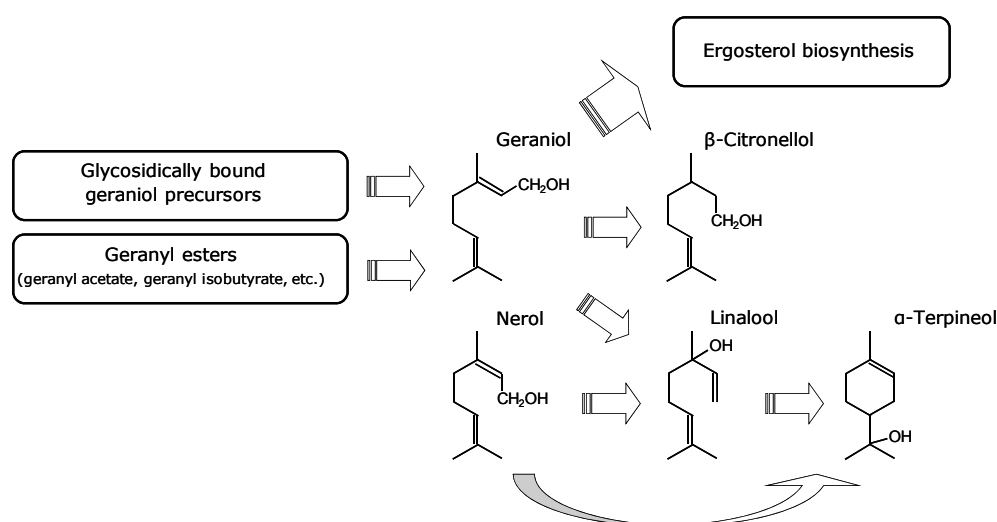
**Fig. 3** Relationship among monoterpene alcohols and their derivatives

In this paper, we measured selected flavour compounds (Figure 1) in late-hopped beers and dry-hopped beers brewed with single hop varieties. On the basis of the results, we discuss the comparison of varietal difference of hop-derived flavour compounds

**Table 3** Compositions of hop-derived flavour compounds in late-hopped and dry-hopped beers made with Hüll Melon, Mandarinina Bavaria and Mosaic

hop variety	Hüll Melon			Mandarinina Bavaria			Mosaic		
	crop	2012			2012			2012	
flavouring hop (g/L of wort)	0.8			0.8			0.8		
hopping procedure	late	dry 1 <sup>a</sup>	dry 2 <sup>a</sup>	late	dry 1 <sup>a</sup>	dry 2 <sup>a</sup>	late	dry 1 <sup>a</sup>	dry 2 <sup>a</sup>
linalool (µg/L)	28.1	16.9	17.0	42.1	26.1	28.2	50.9	34.6	43.1
β-citronellol (µg/L)	15.0	19.1	11.7	17.8	15.6	15.1	24.3	19.5	20.6
nerol (µg/L)	2.9	4.4	4.4	3.1	4.3	6.1	5.1	5.1	6.4
geraniol (µg/L)	8.7	12.9	15.8	9.6	13.2	16.9	13.8	17.1	21.2
geranyl acetate (µg/L)	1.0	2.0	1.2	1.4	2.0	2.0	2.0	2.5	3.6
cis-linalool oxide (µg/L)	5.0	11.2	10.4	1.7	5.8	6.5	1.3	4.7	5.3
β-ionone (µg/L)	0.1	0.2	0.1	0.1	0.2	0.2	tr	0.1	0.2
isobutyl isobutyrate (µg/L)	25.2	26.0	39.5	22.4	19.7	27.8	10.1	9.3	13.6
isoamyl isobutyrate (µg/L)	7.3	8.5	12.2	3.4	3.3	4.6	10.8	11.8	16.3
2-methylbutyl isobutyrate (µg/L)	41.4	42.0	57.0	27.6	24.1	31.6	26.0	22.9	30.9
ethyl heptanoate (µg/L)	3.1	3.3	3.3	4.4	4.7	6.4	5.7	5.4	7.6

a, dry-hopped at 3rd day (dry 1) and 6th day (dry 2) of primary fermentation



**Fig. 4** Biotransformation pathway of monoterpene alcohols by brewing yeast (On the basis of ref. 3, 4, 6, 8, 15, 17, 38–40)

among eighteen hop varieties (Table 1–2), the relationship between certain monoterpene alcohols and their derivatives (Figure 3) and the effect of hopping procedure on the flavour profiles in beers (Table 3).

### 3.2 Comparison of the varietal difference of hop-derived flavour compounds

We brewed test-beers late-hopped with single hop varieties. The U.S. hop varieties (Apollo, Bravo, Citra [32, 33], Mosaic [34] and Summit), the German varieties (Hallertau Blanc, Hüll Melon, Mandarinina Bavaria and Polaris) [35] and the New Zealand varieties (Kohatu, Motueka, Nelson Sauvín [36, 37], Pacific Jade, Rakau, Riwaka, Southern Cross, Wai-iti and Wimea) were used. The compositions of hop-derived flavour compounds, obtained from SPME-GC-MS analysis of these beers, were shown in Table 1 and 2. These compositions differed depending on hop varieties.

Monoterpene alcohols (linalool, β-citronellol and geraniol), their derivatives (geranyl acetate and *cis*-linalool oxide) and esters were widely varied among these eighteen hop varieties. As a result, we thought that these compounds were useful for distinction of “flavour hop” varieties. Of all monoterpene alcohols, the amounts of nerol were smaller than those of other monoterpene alcohols and varied within small range (1.1–5.4 µg/L). β-Ionone was detected at only trace level (max. 0.1 µg/L) in all test-beers. In addition, it has been reported that the thresholds of nerol and β-ionone were at 80 µg/L [3] and 0.6 µg/L [12], respectively.

Therefore, it was thought that the contribution of nerol and β-ionone to the hop varietal difference was smaller than those of other compounds.

Indeed SPME-GC-MS is simple and useful method for analysis of various flavour compounds, a certain category of compounds, for example volatile thiols, could not be analysed by this method. Volatile thiols have been reported as important contributors to the varietal aroma of several flavour hop varieties [13–14, 23–24, 29–31]. We think that the more proper varietal compositions of hop-derived flavour compounds should be constructed with a combination of several analytical methods.

### 3.3 Relationship between certain monoterpene alcohols and their derivatives

Figure 3 shows the scatter plot graphs using the data described in Table 1 and 2. The relationships among geraniol, β-citronellol and geranyl acetate were relatively high. The correlation coefficient

between geraniol and  $\beta$ -citronellol was 0.7325, and that between geraniol and geranyl acetate was 0.8108.

Figure 4 shows the biotransformation pathway of monoterpene alcohols by brewing yeast based on various previous works [3–4, 6, 8, 15, 17, 38–40]. The  $\beta$ -citronellol was almost absent in hop and wort and gently increased during fermentation, because of the biotransformation from geraniol to  $\beta$ -citronellol by yeast [3–4, 6]. Though the free geraniol in initial wort drastically decreases during the first 3–4 days of fermentation [3–4, 6, 8, 38–40], free geraniol could be supplied from glycosidically bound geraniol precursors [3, 6] and/or geranyl esters [8, 15, 17].

The results shown in Figure 3 could support the biotransformation pathway shown in Figure 4. Previous studies have indicated that geraniol contents in finished beer depended on not only initial content of geraniol in wort but also the release of geraniol from precursors (glucosidically bound precursor [3, 6] and/or geranyl esters [8, 15, 17]), and that a part of released geraniol could be transformed to  $\beta$ -citronellol during secondary fermentation period [3, 6].

On the other hand, the relationship between linalool and *cis*-linalool oxide was relatively low (Figure 3). Haley et al. have proposed that linalool oxide might be formed from linalool by oxidative condition during wort boiling and that linalool oxide was detected in late-hopped beer, not in dry-hopped beer [18]. However, our result indicated that the amount of linalool oxide in beer might not depend on the amount of linalool derived from hops. It was assumed that linalool oxide might be contained in raw hop.

### 3.4 Effect of hopping procedure on the flavour profiles in beers

In addition, we brewed test-beers dry-hopped at 3rd day (dry 1) or 6th day (dry 2) of primary fermentation with single hop varieties, Hüll Melon, Mandarina Bavaria and Mosaic. The flavour profiles were compared between late-hopped beer and two dry-hopped beers (Table 3).

Of all monoterpene alcohols, the content of geraniol in the finished beer increased by delaying the timing of the hop addition (dry 1 and dry 2). It is because geraniol was drastically consumed during the yeast growth phase [3–4, 6, 8, 38–40]. In our previous study, the content of geraniol in finished beer could increase by only delaying the timing of hop addition (not dry-hopping), while the yeast growth phase was avoided [6]. The change in other monoterpene alcohols and geranyl acetate were not more significant than that in geraniol. Interestingly, *cis*-linalool oxide increased by dry-hopping. This result could support an occurrence of *cis*-linalool oxide in raw hop.  $\beta$ -Ionone was detected at only trace level (max. 0.2  $\mu$ g/L) in all hopping-conditions. The contents of isobutyric esters and ethyl heptanoate increased by delaying the timing of the hop addition.

## 4 Conclusions

We focused on monoterpene alcohols (linalool,  $\beta$ -citronellol, nerol and geraniol) and their derivatives (geranyl acetate and *cis*-linalool oxide),  $\beta$ -ionone and several esters (isobutyl isobutyrate, isoamyl

isobutyrate, 2-methylbutyl isobutyrate and ethyl heptanoate) as possible contributors on hop varietal aroma. The compositions of these compounds in test-beers brewed with eighteen hop varieties have been analysed and compared.

As a result, the concentrations of linalool,  $\beta$ -citronellol, geraniol, geranyl acetate, *cis*-linalool oxide, isobutyl isobutyrate, isoamyl isobutyrate, 2-methylbutyl isobutyrate and ethyl heptanoate were widely variable among finished beers made with eighteen hop varieties. However, nerol and  $\beta$ -ionone might not almost contribute to the hop varietal difference.

Now, new characteristic hop varieties are continuously bred all around the world. Such hops and beers brewed with these hops are analysed by various approaches. We think that a useful parameter for distinction of hop-derived flavour compounds in beer should show the variation among hop varieties and make a real contribution to the hop-derived varietal aroma in beer. The more proper parameters for hop varietal aromas should be constructed with a combination of several analytical methods suitable for such contributors.

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