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On the Transfer Rate of Geraniol with Dry Hopping

When calculating the transfer rate of geraniol in dry hopped beers based solely on the initial value in hops, there are tremendous fluctuations of between about 40% and over 200%. Some varieties, including Cascade, Hallertau Blanc and Polaris, contain considerable amounts of geranyl acetate in addition to geraniol. However, since no trace of geranyl acetate can be found in the beer, even at high dosages, it can be concluded that at least under these conditions (dry hopping before maturation and storage) geranyl acetate is hydrolyzed and geraniol is released. Including the dosage of geranyl acetate into the calculation of the transfer rates, this yields values of 36 % to 62%, a variation clearly within the limits of error analysis.

Descriptors: hop aroma, dry hopping, transfer rates, geraniol

1 Introduction

A previous work [1] described the fate of hop aroma substances when dry hopping with four new German hop varieties (i.e. Mandarina Bavaria, Huell Melon, Hallertau Blanc and Polaris) with special flavor characteristics. A particularly irritating factor in this study was the behavior of geraniol: "With geraniol things are not clear. Two varieties show a transfer rate of about 50 % and the two others significantly over 100 %. An eye should be kept on this phenomenon." The reported transfer rate of geraniol for Mandarina Bavaria and Huell Melon was 49 %, whereas that of Hallertau Blanc and Polaris was well over 100 %.

The following statement can be found in an earlier paper [2]: "Both geranyl acetate and geranyl isobutyrate were possibly hydrolyzed to geraniol". Especially in Cascade hops geranyl isobutyrate has been detected in considerable amounts and higher levels of geraniol have been found in the corresponding beers [3]. On the basis of these observations the authors concluded the following "It is likely that much of the geraniol found in beer actually originates from the hydrolysis of geranyl isobutyrate rather than from just geraniol in hops." The hydrolysis of geranyl esters has also been reported in other studies [4, 5].

Since in the four new German hop varieties only traces of geranyl isobutyrate, but significantly different levels of geranyl acetate are detected, this study focusses on geranyl acetate in relation to the geraniol content of the final beers. If the geranyl acetate content of the hops is included into the calculation, the transfer rate of geraniol gives a much more defined picture as shown by the results of two test series.

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2 Tests and Results

The first step was to run the test program previously described in [1]. No trace of geranyl acetate could be found in the beers. This lead to the assumption that the geranyl acetate dosage applied by dry hopping before maturation and storage hydrolyzes and geraniol is released. Also in [6] geranyl acetate was found in wort but was no longer present after fermentation. As dry hopped beers were also free of geranyl acetate hydrolysis of geraniol is most likely. Table 1 shows the relevant data in the four hops used.

Whereas two hop varieties have a geranyl acetate content of only 1 mg/100g, the values of the other two varieties are significantly higher at 8 and 17 mg/100g respectively.

Figure 1 shows the proposed hydrolysis of geranyl acetate to geraniol. It is also possible that some still existing esterase activity of the yeast is responsible for this reaction. The molar mass of geraniol is 154.25 g/mol, that of geranyl acetate 196.29 g/mol. Thus a maximum of 0.786 g geraniol can be generated from 1 g geranyl acetate. Table 2 lists the dosages of geraniol and geranyl acetate. In addition, the amount of geranyl acetate is calculated as geraniol via the molar mass. The sum of the original geraniol and that calculated from the concentration of geranyl acetate will be named in the following as "total geraniol".

The content of the control beer is subtracted from the geraniol values in the four beers and the transfer rate by dry hopping is calculated. The reference is the dosage of the original geraniol on the one hand and the dosage of the total geraniol on the other, as shown in Table 3.

Table 1 Content in mg/100g of geraniol and geranyl acetate in 4 hop varieties

Variety	Geraniol	Geranyl acetate
Mandarina Bavaria	14	1
Hüll Melon	8	1
Hallertauer Blanc	2	8
Polaris	4	17

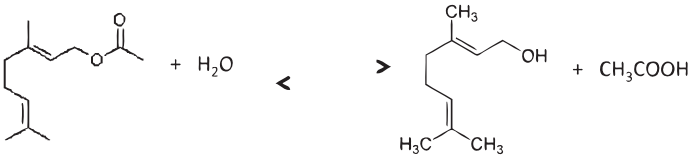

Fig. 1 Proposed hydrolysis of geranyl acetate to geraniol and acetic acid

The maximum range of variation of the transfer rates determined was specified in [1; Table 9] for geraniol as ± 16 % to ± 21 %. If the geraniol values in the beers are related to the total geraniol dosed, transfer rates of 36 % to 55 % are calculated; a variation of ± 10%, which is even less than mentioned above.

In a similarly performed second test, three additional hops were included to the four new varieties. These were Hallertauer Mfr. as well as Cascade grown in the Hallertau and Cascade grown in the USA. Table 4 shows the initial values of geraniol and geranyl acetate in the hops.

Table 5 lists, like table 2, the dosages of geraniol, geranyl acetate and the total geraniol through dry hopping. The dosages for the four new varieties are identical to the first series.

Table 6, like table 3, shows the analysis value for geraniol in the seven beers minus the value in the control beer. In addition it lists the transfer rates of the geraniol referred to the dosage of the original and of the total geraniol. The geraniol values in four beers are similar to those of the first test (Table 3). Identical volumes and procedures for dry hopping lead to comparable values in the beers.

This series also produced relatively similar transfer rates of 38 % to 62 % when the value in the beer is referred to the total geraniol. In [1], also transfer rates for linalool are specified. At over 100 % they are significantly higher than those of geraniol, which can be explained by the release of linalool from glycosidically bound linalool [7]. In the case of geraniol no exact data on corresponding amounts of glycosides are available.

The phenomenon becomes particularly evident when comparing the two varieties Huell Melon and Hallertau Blanc in both series, which show a totally different dosage of geraniol and geranyl acetate (Melon: 82 resp. 8 µg/l; Blanc 18 resp. 72 µg/l). The dosage of total geraniol (free geraniol plus geraniol calculated from geranyl acetate) with 90 µg/l is identical. The resulting yields vary only between 42 and 44 % (Melon) as well as 36 and 47 % (Blanc), which can be regarded as equal keeping in mind analytical errors.

Table 2 Dosages in µg/l of geraniol, geranyl acetate, geraniol calculated from the concentration of geranyl acetate and total geraniol through dry hopping

Variety	Geraniol	Geranyl acetate	Geranyl acetate calc. as geraniol	Total geraniol
Mandarina Bavaria	102	7	6	108
Hüll Melon	82	10	8	90
Hallertauer Blanc	18	91	72	90
Polaris	16	68	53	69

Table 3 Geraniol values in 4 beers (minus control) and the transfer rate with reference only to geraniol and to the total geraniol

Variety	Geraniol µg/l]	Transfer rate % rel. (only geraniol)	Transfer rate % rel. (total geraniol)
Mandarina Bavaria	50	49	46
Hüll Melon	40	49	44
Hallertauer Blanc	32	178	36
Polaris	38	238	55

Table 4 Content in mg/100 g of geraniol and geranyl acetate in 7 hops

Variety	Geraniol	Geranyl acetate
Hallertauer Mfr.	1	0
Mandarina Bavaria	14	1
Hüll Melon	8	1
Hallertauer Blanc	2	8
Polaris	4	17
Hallertauer Cascade	7	15
US Cascade	5	14

Table 5 Dosages in µg/l of geraniol, geranyl acetate and the total geraniol through dry hopping of 7 hops

Variety	Geraniol	Geranyl acetate	Geranyl acetate calc. as geraniol	Total geraniol
Hallertauer Mfr.	13	0	0	13
Mandarina Bavaria	102	7	6	108
Hüll Melon	82	10	8	90
Hallertauer Blanc	18	91	72	90
Polaris	16	68	53	69
Hallertauer Cascade	68	146	115	183
US Cascade	60	168	132	192

Table 6 Geraniol values in 7 beers (minus control) and the transfer rates with reference only to geraniol and to the total geraniol

Variety	Geraniol [µg/l]	Transfer rate % rel. (only geraniol)	Transfer rate % rel. (total geraniol)
Hallertauer Mfr.	5	38	38
Mandarina Bavaria	55	54	51
Hüll Melon	38	46	42
Hallertauer Blanc	42	233	47
Polaris	43	269	62
Hallertauer Cascade	78	114	43
US Cascade	118	197	61

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