Changes in Hop Oil Content and Hoppiness Potential (Sigma) During Hop Aging[1]

Robert T. Foster, II,[2] *Adolph Coors Company, Golden, CO 80401,* **and Gail B. Nickerson,**[3] *Department of Agricultural Chemistry, Oregon State University, Corvallis 97331*

ABSTRACT

This study evaluates the chemical changes in hop oil content and composition during storage of 20 different hop varieties obtained from the hop breeding program at Oregon State University. Chemical analyses of the hop acids and hop oil were performed on mature plants at harvest (fresh) and after a six-month room-temperature stability test (aged). Nineteen main hop compounds for each variety were then calculated to a microliters per kilogram of wort level based on an equal original α-acids hopping rate for comparison. The three groups of hoppy compounds that were derived and totaled were the oxidation products (Σ_{HP}^{OxP}), the floral compounds (Σ_{HP}^{F}), and the citrus compounds (Σ_{HP}^{C}) groups. These three specific hoppiness groups were then totaled, and a total hoppiness potential value (Σ_{HP}^{TOT}) called "Sigma" was derived. Using this sigma value, the 20 different hop varieties were put into four hop categories (aroma, bitter, etc.) based on changes in total hoppiness potential with respect to hop aging.

Key words: α-Acids loss, Hop oil oxidation, Hop varieties, Myrcene loss, Sigma, Total hoppiness potential

There are currently more than 30 hop varieties in commercial production. Many brewers consider the major contributors to beer flavor to be the α-acids (4); however, some breweries still use the traditional low-α-acid European varieties, Hallertau M. F., Hersbrucker, and Tettnang, for their "noble" aroma qualities. Tressel et al and Peacock and Deinzer have indicated that the oxidation products of the sesquiterpenes contribute to "hoppy" aroma (15,17,24). Although there is a great deal of information available about the differences in hop oil composition of different varieties, there are very few reports of the changes that take place during hop storage (9,25).

In this study, 24 hop oil constituents were evaluated for 20 different hop varieties before and after six months of storage. These hops were all obtained from the same experimental yard in Oregon, and all the varieties were mature plants (at least three years old) before picking and chemical analyses. The compounds evaluated are shown in Table I. These compounds were grouped into major hydrocarbons, oxidation products, floral compounds, and citrus compounds.

The steam-distilled oils from 250 g samples of each of the 20 hop varieties were analyzed as described in the experimental section. Correlation coefficients were established for the major flavor groupings with respect to percent original α-acids, hop storage index (HSI), percent α-acids remaining, hop oil (ml/100 g of hops), and myrcene (μl/g of original α-acids). The hop varieties that were statistically analyzed in this manner are listed in Table II.

The calculations used to determine the microliters of each compound or compound group per gram of α-acids are described in the experimental section. These values are based on the calculated "original" α-acids level (α_o) that a brewer would use to adjust the hopping rate to an equal α-acids dosage for bitterness control in final beer. The calculation to an equal α_o and the subsequent grouping of similar flavor compounds present in the hop oil was done to simulate the type of beer hoppy flavor a brewer might expect from those 20 different hop varieties if they were used both fresh and aged. The flavor grouping of compounds was done according to our perception of their flavor impact.

[1]Presented at the 50th Annual Meeting, St. Louis, MO, September, 1984.
[2]Senior Research Associate.
[3]Chemist.

The floral group consists of the total μl/g α_o of geranyl acetate, geranyl isobutyrate, geraniol, and linalool (Table I). These compounds have been grouped because studies by Tressel et al and by Peacock and Deinzer have shown the survival of these floral compounds to final beer (16,24). Even though the flavor thresholds of these compounds in beer are different, the total floral aroma and flavor is probably additive and synergistic. This idea was suggested by Peacock et al in an attempt to calculate a "floral index" for various hop varieties (16). This same reasoning led us to group the oxidation products of α-humulene and β-caryophyllene along with an additional group of compounds with citrus-like flavors. The μl/g α_o of each compound within a group were totaled, and the totals for each of the three flavor groups—oxidation products, floral compounds, and citrus compounds—were then evaluated in these 20 varieties, both fresh and aged.

EXPERIMENTAL

Sample Preparation

Hop samples used for varietal comparisons were obtained from the experimental Hop Yard at the Oregon State University Agricultural Experiment Station, Corvallis, OR. Samples were machine picked and dried in 10-cm-deep trays at 45°C for 8 hr. The trays of dried hops were equilibrated at 55% relative humidity overnight and then pressed into miniature hop bales of 600–800 g (20 × 15 × 10 cm) and refrigerated. The "fresh" sample, about 300 g, was frozen until analysis. Part of the sample was ground to determine moisture content (1) and for spectrophotometric determination of α- and β-acids (2). The "aged" sample, about 300 g, was sealed in a plastic bag, stored at room temperature in the dark, and after six months placed in frozen storage until analysis (Fig. 1).

Approximately 250 g of whole hops was placed in a 12-L flask containing 5 L of 0.01*M* sodium phosphate, pH 6.0, buffer and distilled for 6 hr, using a Wright and Connery oil trap (26). The amount of hop oil collected was measured volumetrically and the oil transferred to glass ampoules and sealed. The ampoules were held at 20°C until gas-liquid chromatography analysis.

Gas Chromatographic Analysis

A Hewlett-Packard 5830A gas chromatograph equipped with capillary column, inlet splitter (1:100), automatic sample injector, and flame-ionization detector was used for analysis and quantitation. The column was a 30-m glass capillary coated with SP 1000. Helium was used as the carrier gas. Temperatures were: detector, 250°C; inlet, 230°C (10). The oven temperature was programmed to a final temperature of 190°C. Typical hop oil chromatograms are shown in Figure 2. Identification of the individual peaks of interest was verified by gas chromatography/mass spectrophotometry, and retention times were confirmed by spiking hop oil samples with reference compounds.

Quantitation of Results

The percent α- and β-acids remaining was calculated using the following formula:

$$\% \, \alpha\text{- } + \beta\text{-acids remaining} = 100 - 100 \left(\log \frac{\text{HSI}}{0.24}\right).$$

HSI (the hop storage index) is the ultraviolet absorbance at 275 nm divided by absorbance at 325 nm. The HSI is then divided by a constant, 0.24, which is the average HSI for fresh hops (12). The percent α- and β-acids remaining was used to calculate the original α-acids content (19):

$$\% \alpha_o = \frac{\text{Apparent } \% \alpha\text{-acids}}{\% \alpha\text{- + } \beta\text{-acids remaining}} \times (100).$$

The oil content (ml oil/100 g of dried hops) and the percent α- and β-acids were calculated on an 8% moisture basis for all 20 hop varieties.

After the α_o, milliliters of oil/100 g of hops, and percent chromatographic peak area of a particular compound in the hop oil were found, then the microliters of each compound were calculated per gram α_o. This was necessary because the percent α_o for these 20 varieites ranged from 5.0–14.8%. More important, the brewer would want to control the bitterness units (BU) in the beer by trying to control the pounds of original α-acids added to the wort. Thus, a standardization of each compound in the hop oil with respect to grams α_o is necessary for a realistic comparison of these 20 hop varieties.

Calculation:

μl Compound/g α_o

$$= \frac{\text{ml oil/100 g hops}}{\% \alpha_o} \times \frac{\% \text{ Peak area of each}}{\text{compound in oil}} \times 10.$$

Example: Willamette

$$\% \alpha \text{ apparent} = 6.6\% \quad \text{(ASBC [2])}$$
$$\text{HSI} = 0.287 \quad \text{(Likens [12])}$$
$$\text{ml Oil/100 g hops} = 0.88$$
$$\% \text{ Myrcene area in oil} = 33.2\%$$

$$\% \alpha\text{- + } \beta\text{-Acid remaining} = 100 - 100 (\log \frac{0.287}{0.240}) = 92.2\%$$

$$\alpha_o = (\frac{6.6\%}{92.2\%})(100) = 7.16\%$$

$$\mu\text{l Myrcene/g } \alpha_o = (\frac{0.88}{7.16})\ 33.2\% \times 10 = 40.79.$$

All the chemical data were analyzed statistically using a Hewlett-Packard 9845B computer and a BASIC statistics package. A standard statistical table (23) was used to determine significance levels.

RESULTS AND DISCUSSION

Aging Changes with Respect to Hop Oil, Myrcene, and α-Acids

Table II lists the hop varieties and some of the chemical data evaluated. As seen in Figure 3, the higher the fresh apparent α-acids

TABLE I
Hop Oil Compounds by Flavor Grouping

Major Hydrocarbons	Oxidation Products	Floral Compounds	Citrus Compounds
β-Pinene	Caryophyllene epoxide	Geranyl acetate	Limonene
Myrcene	Caryolan-1-ol	Geranyl isobutyrate	Citral
β-Caryophyllene	Humulene monoepoxide I	Geraniol	Cadinene
Farnesene	Humulene monoepoxide II	Linalool	Nerol
α-Humulene	Humulene monoepoxide III		Limonen-10-ol
	Humulene diepoxide A		
	Humulene diepoxide B		
	Humulene diepoxide C		
	Humulenol II		
	Nerolidol		

TABLE II
Chemical Profile of 20 Different Hop Varieties

	Original % α-Acids[a]		Apparent % α-Acids[b]		Oil (ml)/100 g Hops		Myrcene μl/g α_o	
Variety	Fresh	Aged	Fresh	Aged	Fresh	Aged	Fresh	Aged
Eroica	14.8	13.4	14.3	9.7	1.13	0.54	39.45	6.24
Wye Target	13.7	12.0	13.5	7.2	1.93	0.57	78.72	5.76
Nugget	12.6	11.5	12.0	9.5	1.26	0.63	42.55	13.09
Blisk	12.4	10.3	12.0	6.7	1.38	0.87	46.12	16.13
Galena	11.0	10.5	10.8	9.1	0.76	0.55	22.03	13.31
Perle	11.3	10.9	10.6	8.7	1.08	0.67	32.80	15.98
Olympic	10.6	9.3	10.6	6.6	0.86	0.26	32.37	6.78
Record	10.7	9.3	10.2	6.5	1.32	0.74	49.20	8.20
Wye Challenger	9.7	9.4	8.8	8.3	1.00	0.62	36.85	10.90
Columbia	9.1	8.4	8.8	7.2	0.49	0.19	16.72	0.29
Brewer's Gold	9.2	8.8	8.7	6.4	1.52	0.43	86.12	9.80
Hersbrucker	7.1	6.4	7.4	4.3	0.92	0.57	55.12	15.84
Kirin II	6.9	6.0	6.9	4.6	1.11	0.66	63.46	25.21
Willamette	7.2	6.4	6.6	5.1	0.88	0.43	40.79	14.88
Tettnang	6.9	6.2	6.6	4.1	0.96	0.64	70.35	31.30
Hallertau M. F.	6.5	5.9	6.1	4.1	1.11	0.42	91.95	15.92
Cluster	5.9	5.2	5.7	4.7	0.27	0.17	15.88	4.70
Styrian	6.2	5.7	5.5	4.0	0.50	0.24	22.50	4.46
Cascade	5.7	4.5	4.9	2.7	0.90	0.09	86.61	3.16
Fuggle	5.0	4.5	4.5	3.2	0.69	0.36	47.86	14.55

[a] Rehberger and Bradlee (19).
[b] ASBC spectrophotometric α-acids analyses (as-is basis).

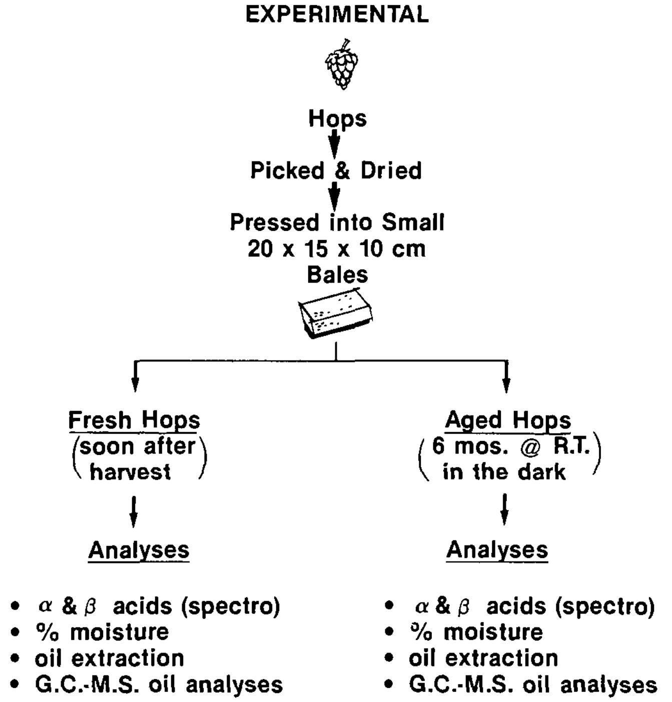

Fig. 1. The aging scheme and chemical analyses of the hop oil from 20 hop varieties.

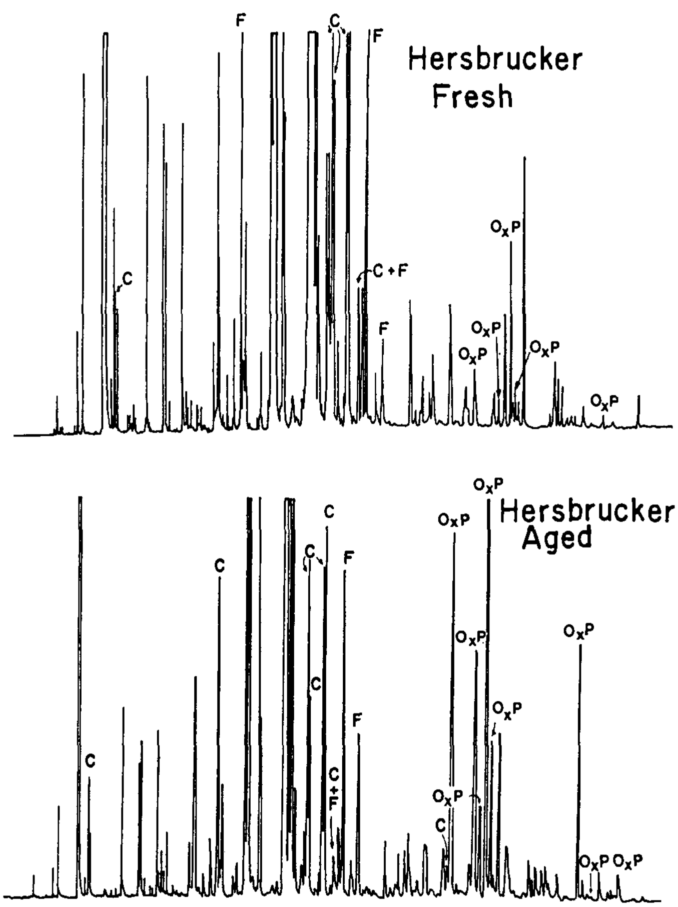

Fig. 2. A typical gas chromatogram for Hersbrucker fresh hop oil, **top**, and after six months of aging at room temperature in the dark, **bottom**. **C** = Citrus compounds, **F** = floral compounds, and **OxP** = oxidation products of α-humulene and β-caryophyllene.

level in these 20 hop varieties, the higher the oil content. This relationship is significant at the 1% level and has a correlation coefficient of $r = 0.595$. Also, as reported in the literature (7), the higher the oil content in the hop variety, the higher the amount of myrcene/g α_o. This relationship has a correlation coefficient of 0.626 and is significant at the 1% level (Fig. 4).

When the myrcene and hop oil levels in aged hops are subtracted from those in fresh hops, the difference is the μl/g α_o myrcene loss versus milliliters of hop oil loss with respect to hop aging (Table III). Because the largest component of hop oil is usually myrcene, a greater loss of myrcene would cause a greater loss in the total hop oil when aged (Fig. 5). The correlation coefficient between myrcene loss and oil loss (ml) is $r = 0.693$, significant at the 1% level. This relationship between loss of myrcene and total hop oil has also been reported in the literature (17,18).

As shown several times in the literature (3,7,13,18), the loss in percent α-acids apparent shows a significant relationship with myrcene loss μl/g α_o. The correlation coefficient for this relationship is $r = 0.505$, significant at the 5% level (Fig. 6). This relationship indicates that hop varieties showing a large drop in the myrcene level in the hop oil from fresh to aged may also have a greater drop in percent of α-acids apparent. In addition, a correlation coefficient of $r = 0.687$, significant at the 1% level, is seen when graphing μl/g α_o myrcene in fresh hops versus HSI in

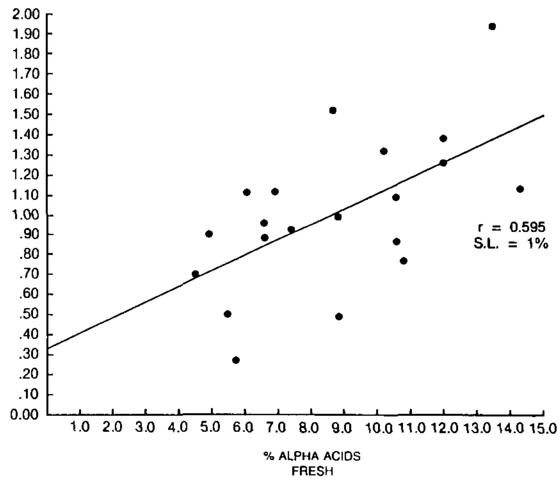

Fig. 3. Comparison of hop oil (ml/100 g hops) in 20 hop varieties with the percent α-acids level in fresh hops (as determined by ASBC spectrophotometric method (2) ($r = 0.595$ at the 1% significance level).

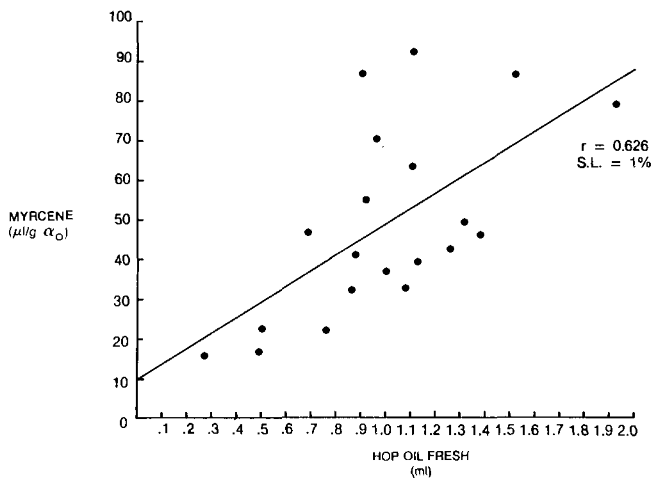

Fig. 4. Comparison of the myrcene level (μl/g α_o) versus the hop oil level (ml/100 g hops) in fresh hops ($r = 0.626$ at the 1% significance level).

aged hops (Fig. 7). This relationship indicates that myrcene may have a role in the oxidation of α-acids during hop storage. This theory has been suggested in the literature several times even though the actual catalytic mechanism, if it exists, appears to be unknown (3,7,13,18).

It has been reported several times in the literature that myrcene and β-pinene do not survive the kettle boil (8,11,21,22). Therefore, myrcene, the largest component in the hop oil, does not contribute to hoppy character in final beer, with the exception that myrcene can possibly break down to several other flavor-active compounds, as reported by Dieckmann and Palamand (5) (Fig. 8). It has also been reported that β-caryophyllene, farnesene, and α-humulene survive neither fermentation nor absorption on filter mass (22). Therefore, they now become unimportant as direct contributors to final beer flavor. Of the four groups listed in Table I, only three remain important when the major hydrocarbon group is eliminated, and they are the oxidation products, the floral compound, and the citrus compound groups.

Aging Changes with Respect to Hoppiness Potential Groupings

The compounds that remain flavor active and do survive the hop oil oxidation, brewing kettle boil, fermentation, and filtration are the oxygenated epoxides of α-humulene and β-caryophyllene and the floral compounds (14,15,16,17,24). Beer sometimes has a citrus/fruity flavor. For this reason, the citrus compounds are grouped and added to this evaluation even though the chemistry showing their breakdown products and survival in beer is largely unknown (Table I).

A significant (5% level) correlation of $r = 0.506$ exists between the $\mu l/g\ \alpha_o$ of α-humulene in a hop variety when fresh and the level of oxidation products of α-humulene in the aged hops (Fig. 9). A scheme for the oxidation of α-humulene is shown in Figure 10 (P. Lam and M. Deinzer, *personal communication*). Roberts (20) first demonstrated the autoxidation of β-caryophyllene to caryophyllene epoxide. Caryophyllene epoxide has also been found in beer

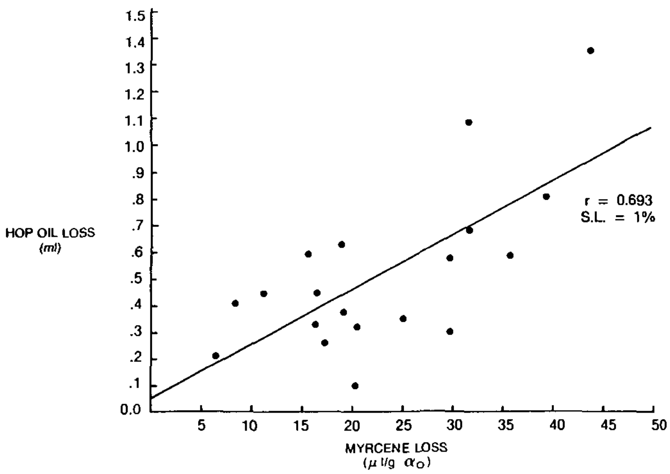

Fig. 5. Comparison of the hop oil loss (ml/100 g hops) versus the myrcene loss ($\mu l/g\ \alpha_o$) during hop aging ($r = 0.693$ at the 1% significance level).

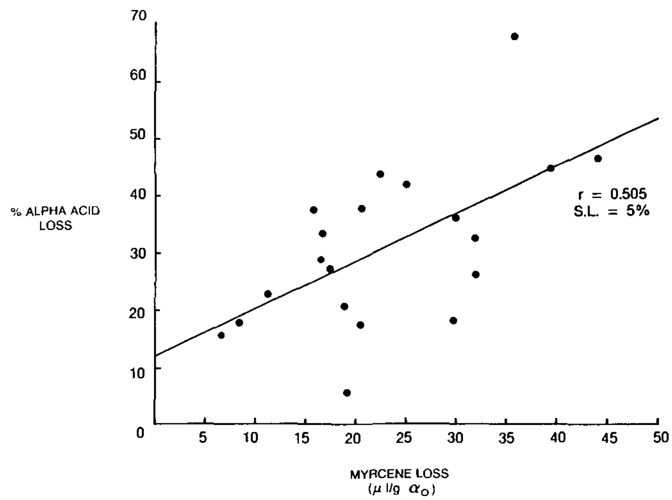

Fig. 6. Percent α-acid loss (apparent) versus the myrcene loss ($\mu l/g\ \alpha_o$) with respect to hop aging ($r = 0.505$ at the 5% significance level).

TABLE III
Hop Oil and α-Acids Chemical Changes of 20 Different Hop Varieties with Respect to Aging

Variety	Oil Loss (ml)	Myrcene Loss $\mu l/g\ \alpha_o$	% α-Acids Loss (Apparent)[a]	Myrcene $\mu l/g\ \alpha_o$ Fresh Hops	Hop Storage Index Aged Hops
Hallertau M. F.	0.69	76.03	2.0	91.95	0.50
Cascade	0.81	83.45	2.2	86.61	0.63
Brewer's Gold	1.09	76.32	2.3	86.12	0.47
Wye Target	1.36	72.96	6.3	78.72	0.63
Tettnang	0.32	39.05	2.5	70.35	0.55
Kirin II	0.45	38.25	2.3	63.46	0.43
Hersbrucker	0.35	39.28	3.1	55.12	0.53
Record	0.58	41.08	3.7	49.20	0.50
Fuggle	0.33	33.31	1.3	47.86	0.48
Blisk	0.51	30.00	5.3	46.12	0.56
Nugget	0.63	29.45	2.5	42.55	0.37
Willamette	0.45	25.92	1.5	40.79	0.40
Eroica	0.59	33.02	4.6	39.45	0.47
Wye Challenger	0.38	25.96	0.5	36.85	0.33
Perle	0.41	16.82	1.9	32.80	0.40
Olympic	0.60	25.59	4.0	32.37	0.49
Styrian	0.26	18.05	1.5	22.50	0.49
Galena	0.21	8.72	1.7	22.03	0.34
Columbia	0.30	16.43	1.6	16.72	0.35
Cluster	0.10	11.18	1.0	15.88	0.31

[a] ASBC spectrophotometric α-acids analyses (as-is basis).

(15,17,24) and in this evaluation is considered part of the oxidation products group.

The relationship between total $\mu l/g\ \alpha_0$ citrus compounds from fresh hops versus total $\mu l/g\ \alpha_0$ citrus compounds from aged hops was significant (1% level), with a correlation coefficient of 0.963 (Fig. 11). This indicates that if a particular hop variety is high in citrus flavor compounds when fresh compared to another fresh variety, these compounds will probably remain at their same relative levels in the aged hops. It may be interesting to note the high level of citrus compounds found in Kirin II; the citrus-compound level is five times greater than the average for both fresh and aged samples of all 20 hop varieties (Table IV).

Similarly, total $\mu l/g\ \alpha_0$ of floral compounds in fresh hops is significantly (1% level) correlated with total floral compounds in the aged hops, with $r = 0.724$ (Fig. 12).

These relationships between the three hoppy flavor groups (oxidation products, floral compounds, and citrus compounds) and hop aging indicate that, depending on what type of hoppy flavor a brewer may want in production beer, he may choose a type of hops containing high or low levels of the desired hop flavor compounds. If a brewer selects hops high in floral or citrus compounds, they will remain relatively the same in the aged hops (Table IV). Brewers desiring hops with a high level of the oxidation products of α-humulene and β-caryophyllene for their beer would choose hops high in these two compounds that oxidize at a fairly steady rate.

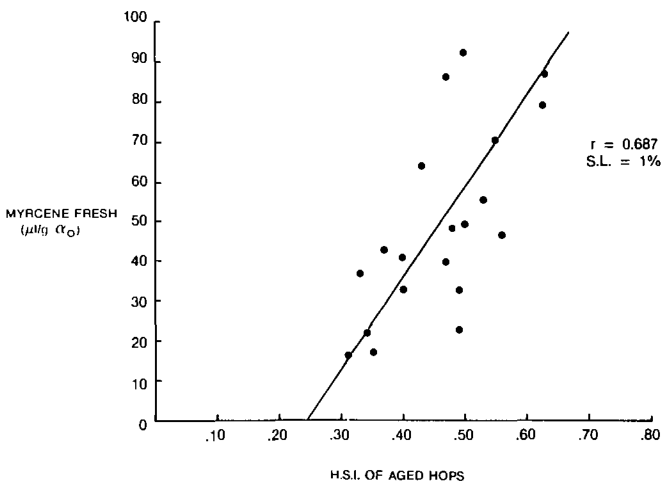

Fig. 7. The myrcene level ($\mu l/g\ \alpha_0$) in fresh hops versus the hop storage index (HSI) of aged hops ($r = 0.687$ at the 1% significance level).

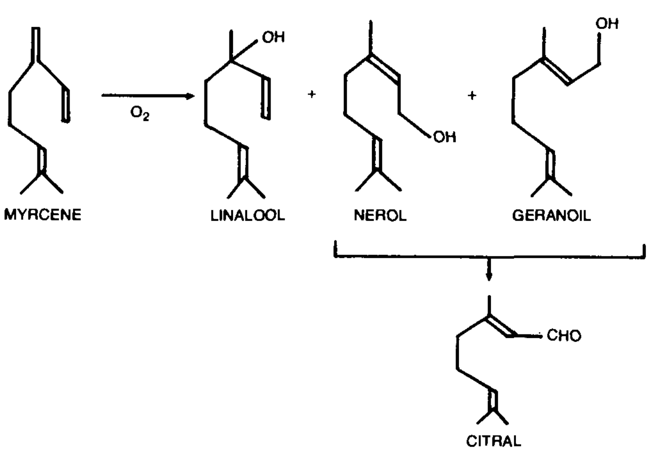

Fig. 8. The air oxidation products of myrcene. [Reprinted with permission from Dieckmann, R. H., and Palamand, S. R. *J. Agric. Food Chem.* 22(3):498, 1974. Copyright 1974 American Chemical Society.]

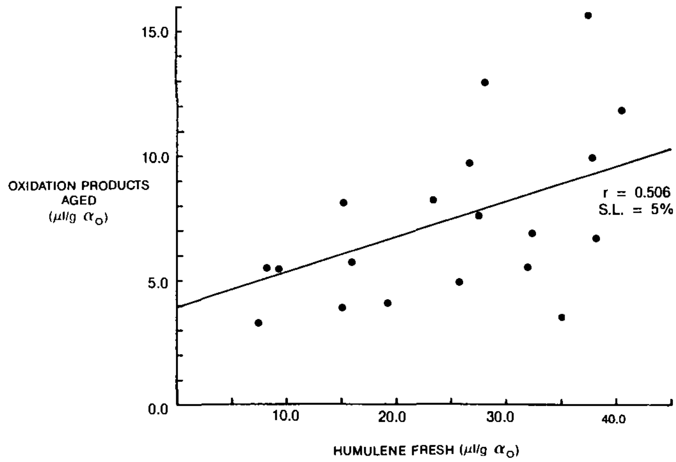

Fig. 9. The oxidation products group ($\mu l/g\ \alpha_0$) in aged hops versus the α-humulene level ($\mu l/g\ \alpha_0$) in fresh hops ($r = 0.506$ at the 5% significance level).

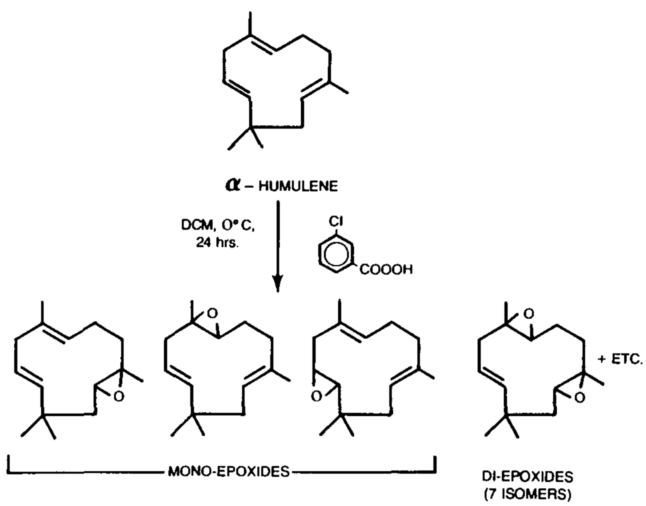

Fig. 10. The oxidation scheme of α-humulene to the mono- and diepoxides (P. Lam and M. Deinzer, Oregon State University, *personal communication*).

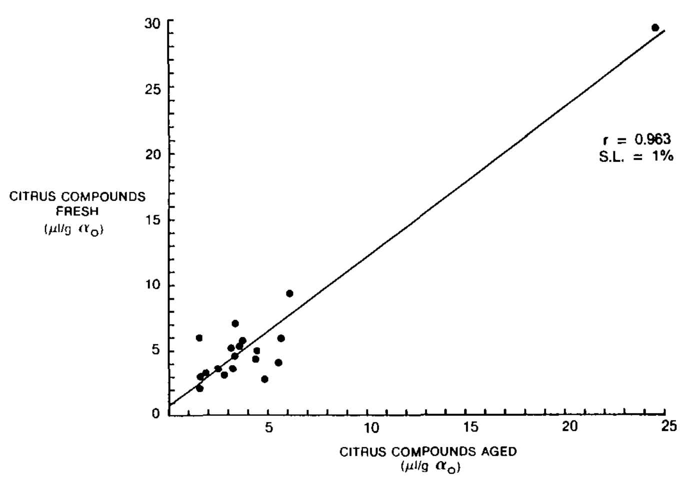

Fig. 11. Comparison of the citrus compound group ($\mu l/g\ \alpha_0$) in fresh versus aged hops ($r = 0.963$ at the 1% significance level).

A relationship exists between the change in $\mu l/g\ \alpha_o$ of the oxidation products group compared to the total $\mu l/g\ \alpha_o$ of all three flavor groups during hop aging (Table V). This suggests that as the hop ages, the change in the total $\mu l/g\ \alpha_o$ of the three flavor groups is primarily attributed to changes in the oxidation products group alone. This relationship shows a correlation coefficient of $r = 0.929$, which is significant at the 1% level (Fig. 13).

Hoppiness Potential or "Sigma" Changes with Aging

To put this flavor grouping technique in perspective as to what kind of "hoppiness potential" (Σ_{HP}) or sigma each of these 20 hop varieties would have in beer, an equal original α-acids hopping rate was calculated based on a model brewery. The model brewing kettle has a capacity of 750 bbl and the kettle fill is 14° Plato. Let us say that the brewer empirically knows 16.4 lb of "original" α-acids added to the brewing kettle is needed to arrive at a desired 16 BU in the packaged beer. Because all the components in the hop oil, both fresh and aged, have been standardized to microliters of original α-acids, the total contribution of each compound and flavor group can easily be calculated.

Data needed: 1) Brewing kettle capacity = 750 bbl. 2) Brewing kettle fill °P = 14°P or 38.17 lb extract/bbl (value was obtained from the Schwartz Laboratories Extract Table). 3) Pounds α_o needed to maintain a 16 BU in finished beer = 16.4 lb. 4) Oxidation products level of Hersbrucker hop oil, aged = 15.65 $\mu l/g$ original alpha (α_o). These data are included in an example calculation for Hersbrucker hops aged (Σ_{HP}^{OxP}):

Oxidation products group "hoppiness potential"

$$(\Sigma_{HP}^{OxP})\ \mu l/kg\ \text{wort} = \frac{16.4\ \text{lb}\ (\alpha_o) \times 453.59\ \text{g/lb} \times 15.65\ \mu l/g\ \alpha_o}{\dfrac{(750\ \text{bbl} \times 38.17\ \text{lb extract/bbl})}{2.2046\ \text{lb/kg}}}$$

$$= \frac{7{,}439\ \text{g}\ \alpha_o\ \text{needed} \times 15.65\ \mu l/g\ \alpha_o\ \text{Ox. prod.}}{12{,}985.3\ \text{kg wort}}$$

$$\Sigma_{HP}^{OxP} = \frac{8.97\ \mu l\ \text{Oxidation products group}}{\text{kg wort}}.$$

This calculation shows how to standardize the oxidation products of Hersbrucker aged hops to a kilogram of wort basis. Once it is standardized to a constant wort or hopping rate basis, the hoppiness potential of the oxidation products flavor group is given the symbol sigma, Σ_{HP}^{OxP}. The hoppiness potential was then computed for each of the 20 varieties for each of the three hoppy flavor groups (oxidation products Σ_{HP}^{OxP}, floral compounds Σ_{HP}^{F}, and citrus compounds Σ_{HP}^{C}), both fresh and aged.

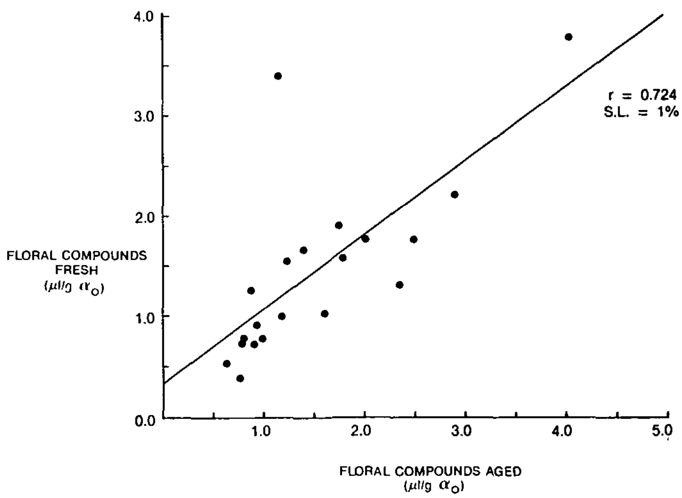

Fig. 12. Comparison of the floral compound group ($\mu l/g\ \alpha_o$) in fresh versus aged hops ($r = 0.724$ at the 1% significance level).

TABLE IV
Hop Oil Flavor Groupings of 20 Different Hop Varieties Both Fresh and Aged

Variety	Humulene $\mu l/g\ \alpha_o$ Fresh	Oxidation Product Compounds $\mu l/g\ \alpha_o$ Fresh	Oxidation Product Compounds $\mu l/g\ \alpha_o$ Aged	Citrus Compounds $\mu l/g\ \alpha_o$ Fresh	Citrus Compounds $\mu l/g\ \alpha_o$ Aged	Floral Compounds $\mu l/g\ \alpha_o$ Fresh	Floral Compounds $\mu l/g\ \alpha_o$ Aged
Fuggle	40.46	4.08	11.82	5.71	3.75	1.66	1.40
Record	38.16	2.03	9.93	4.10	5.53	1.03	1.60
Willamette	38.10	1.54	6.74	5.19	3.22	0.73	0.91
Hersbrucker	37.38	1.28	15.65	4.35	4.38	2.21	2.90
Perle	34.99	1.09	3.52	3.61	2.53	0.73	0.78
Hallertau M. F.	32.24	1.30	6.92	3.58	3.22	1.00	1.18
Brewer's Gold	31.91	1.64	5.55	7.10	3.39	1.26	0.87
Tettnang	28.13	2.18	12.91	5.51	3.57	1.77	2.49
Styrian	27.47	2.40	7.62	3.24	1.82	0.78	0.98
Kirin II	26.57	1.83	9.68	29.40	24.56	3.79	4.06
Nugget	25.62	1.25	4.95	4.58	3.34	0.90	0.93
Wye Challenger	23.37	4.51	8.23	13.30	11.14	1.90	1.76
Cascade	19.17	8.11	4.10	5.99	1.55	3.40	1.15
Wye Target	15.86	1.81	5.72	9.30	6.07	1.58	1.77
Columbia	15.19	1.16	3.90	2.22	1.51	0.54	0.63
Blisk	15.13	1.12	8.14	2.81	4.82	1.32	2.36
Cluster	9.30	1.58	5.48	3.10	2.76	0.78	0.80
Galena	8.25	7.24	5.48	5.00	4.44	1.55	1.23
Olympic	7.37	1.27	3.27	3.04	1.56	0.38	0.78
Eroica	0.51	3.00	6.40	5.95	5.68	1.76	2.01
$\overline{X}$	23.74	2.52	7.30	6.35	4.94	1.45	1.53

As seen in Table VI, Cascade and Galena hops appear to be at their highest levels for the oxidation products group (Σ_{HP}^{OxP}) when they are fresh. This suggests that Cascade hops are at their best when they are fresh, which has been reported by this author in the past (6). This ranking of Cascade at the top of the oxidation products list when fresh and close to the bottom when aged supports the earlier finding. Cascade and Galena were the only varieties with oxidation products group levels that fell upon aging. In contrast, varieties Hersbrucker, Blisk, Tettnang, Hallertau M. F., Kirin II, Record, and Willamette show large increases in the oxidation products group in aged hops. This strongly suggests that a brewer interested in the sesquiterpene oxidation products, also called the "noble" aroma compounds, age these hop varieties before brewing to enhance their contribution to final beer flavor. Other varieties that deserve mention for their high level of oxidation products are Fuggle, Wye Challenger, and Styrian.

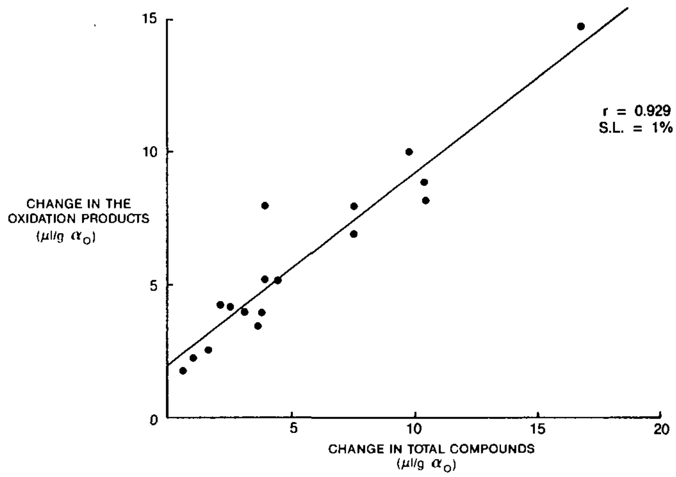

Fig. 13. Changes in the oxidation products group (μl/g α_0) versus changes in the total hoppiness potential of all three groups (oxidation products, floral, and citrus) with hop aging ($r = 0.929$ at the 1% significance level).

TABLE V
Changes in the Microliters per Gram Original α-Acids (μl/g α_0) for the Oxidation Products Group Compared to Changes for the Total for All Three Hoppy Compound Groups with Respect to Hop Aging

Variety	Δ μl/g α_0 Oxidation Products Group	Δ μl/g α_0 Total Compounds
Hersbrucker	14.37	15.09
Tettnang	10.73	9.51
Record	7.90	9.90
Kirin II	7.85	3.28
Fuggle	7.74	5.52
Blisk	7.02	10.07
Hallertau M. F.	5.62	5.44
Styrian	5.22	4.00
Willamette	5.20	3.41
Wye Target	3.91	0.87
Brewer's Gold	3.91	0.02
Cluster	3.90	3.59
Wye Challenger	3.72	1.42
Nugget	3.70	2.49
Eroica	3.41	3.39
Columbia	2.74	2.12
Perle	2.43	1.40
Olympic	2.00	0.92
Galena	−1.76	−2.64
Cascade	−4.01	−10.70

Table VII shows the difference in hoppiness potential of floral compounds (Σ_{HP}^{F}) in the model brewery hopping calculation before and after aging. Galena and, especially, Cascade show a similar trend for floral compounds as seen in the oxidation products group. Cascade has the second highest floral contribution when fresh and upon aging loses the greatest amount of all 20 varieties. This again indicates that Cascade is at the best level of hoppiness potential when fresh. Galena and Brewer's Gold show the same trend downward in floral contribution with age.

In contrast, Kirin II, Hersbrucker, Tettnang, Blisk, and Record show increases in floral compounds with subsequent aging. Other varieties that showed increases in the floral compound level after aging were Eroica and Wye Target. After aging, Wye Challenger dropped slightly in the floral compound group but was still at a relatively high level.

The citrus compounds group (Table VIII) shows an overall loss in total citrus compounds (Σ_{HP}^{C}) with aging for most of the varieties.

TABLE VI
Comparison of the Contribution of the Oxidation Products Group to a Model Brew Wort, Before and After Aging 20 Hop Varieties

Fresh		Aged	
μl/kg Wort	Variety	μl/kg Wort	Variety
4.66	Cascade	8.97	Hersbrucker
4.16	Galena	7.42	Tettnang
2.59	Wye Challenger	6.79	Fuggle
2.34	Fuggle	5.70	Record
1.72	Eroica	5.56	Kirin II
1.38	Styrian	4.73	Wye Challenger
1.25	Tettnang	4.68	Blisk
1.17	Record	4.38	Styrian
1.05	Kirin II	3.98	Hallertau M. F.
1.04	Wye Target	3.87	Willamette
0.94	Brewer's Gold	3.68	Eroica
0.91	Cluster	3.29	Wye Target
0.88	Willamette	3.19	Brewer's Gold
0.75	Hallertau M. F.	3.15	Cluster
0.74	Hersbrucker	3.15	Galena
0.73	Olympic	2.84	Nugget
0.72	Nugget	2.36	Cascade
0.67	Columbia	2.24	Columbia
0.64	Blisk	2.02	Perle
0.63	Perle	1.88	Olympic

TABLE VII
Comparison of the Contribution of the Floral Group to a Model Brew Wort, Before and After Aging 20 Hop Varieties

Fresh		Aged	
μl/kg Wort	Variety	μl/kg Wort	Variety
2.18	Kirin II	2.33	Kirin II
1.95	Cascade	1.67	Hersbrucker
1.27	Hersbrucker	1.43	Tettnang
1.09	Wye Challenger	1.36	Blisk
1.02	Tettnang	1.15	Eroica
1.01	Eroica	1.02	Wye Target
0.95	Fuggle	1.01	Wye Challenger
0.91	Wye Target	0.92	Record
0.89	Galena	0.80	Fuggle
0.76	Blisk	0.71	Galena
0.72	Brewer's Gold	0.68	Hallertau M. F.
0.59	Record	0.66	Cascade
0.57	Hallertau M. F.	0.56	Styrian
0.52	Nugget	0.53	Nugget
0.45	Styrian	0.52	Willamette
0.45	Cluster	0.50	Brewer's Gold
0.42	Willamette	0.46	Cluster
0.42	Perle	0.45	Olympic
0.31	Columbia	0.45	Perle
0.22	Olympic	0.36	Columbia

Again, Cascade has a high citrus compound level when fresh and then drops to one of the lowest when aged. Brewer's Gold showed a similar trend. Kirin II actually lost more from the citrus compound group than any other variety; however, its citrus compound level was so high to begin with (five times greater than the average, Table IV) that even after aging, Kirin II remained the number one hop variety for citrus compounds. Two other hop varieties, Blisk and Record, gained in citrus compounds upon aging.

Hop Varieties Categorization by Hoppiness Potential (Sigma)

Not only may each of these three hoppy flavor groups have an individual effect on beer flavor, but they may have an additive or synergistic effect on final beer hoppiness, so a total hoppiness potential or sigma value calculation was devised. The total μl/kg wort hoppiness potential calculation is a grand sum of all three individual flavor groups: The total sum of the ten oxidation products (Σ^{OxP}_{HP}) + the total sum of the four floral compounds (Σ^{F}_{HP}) + the total sum of the five citrus compounds (Σ^{C}_{HP}) = the total sum of the hoppiness potential (sigma), or $\Sigma^{TOT}_{HP} = \Sigma^{OxP}_{HP} + \Sigma^{F}_{HP} + (\Sigma^{C}_{HP})$.

In looking at the changes in total hoppiness potential with respect to hop aging, four categories became apparent (Table IX).

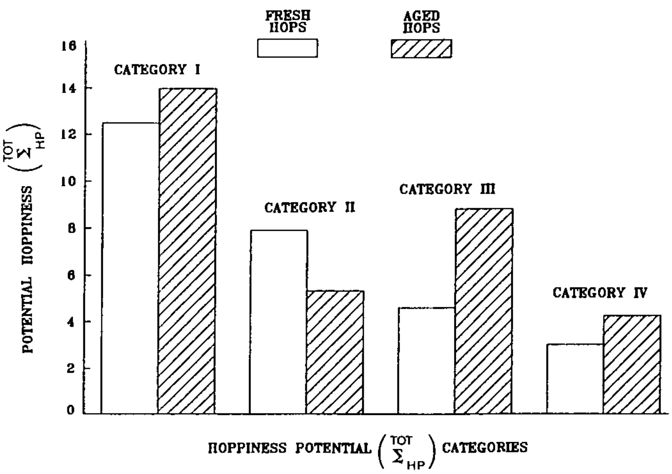

Fig. 14. The categorization of hop variety type by total hoppiness potential, or sigma, in both fresh and aged hops.

TABLE VIII
Comparison of the Contribution of the Citrus Group to a Model Brew Wort, Before and After Aging 20 Hop Varieties

Fresh		Aged	
μl/kg Wort	**Variety**	**μl/kg Wort**	**Variety**
16.89	Kirin II	14.11	Kirin II
7.64	Wye Challenger	6.40	Wye Challenger
5.34	Wye Target	3.49	Wye Target
4.08	Brewer's Gold	3.26	Eroica
3.44	Cascade	3.18	Record
3.42	Eroica	2.77	Blisk
3.28	Fuggle	2.55	Galena
3.17	Tettnang	2.52	Hersbrucker
2.98	Willamette	2.15	Fuggle
2.87	Galena	2.05	Tettnang
2.63	Nugget	1.95	Brewer's Gold
2.50	Hersbrucker	1.92	Nugget
2.36	Record	1.85	Willamette
2.07	Perle	1.85	Hallertau M. F.
2.06	Hallertau M. F.	1.59	Cluster
1.86	Styrian	1.45	Perle
1.78	Cluster	1.05	Styrian
1.75	Olympic	0.89	Cascade
1.61	Blisk	0.87	Columbia
1.28	Columbia	0.86	Olympic

Category I shows the hop varieties that exhibit a very high total hoppiness (μl/kg wort) level when fresh and maintain this high level (sigma) after aging. These hops, Kirin II, Wye Challenger, and Wye Target, even show a slight increase in total hoppiness potential levels in wort with aging.

In category II, Cascade, Galena, and Brewer's Gold show a high hoppiness level to be imparted into the wort from fresh hops. However, this level decreases when the hops are aged. If a brewer wishes to get the most hoppiness from these three varieties, then they should be as fresh as possible when used and stored under very cold conditions.

Category III hops show a trend opposite to hops in category II. Nine varieties—Hersbrucker, Tettnang, Record, Fuggle, Blisk, Eroica, Hallertau M. F., Willamette, and Styrian—all show a relatively low level of hoppiness potential when fresh. However, the total hoppiness potential (sigma) imparted to the wort appears to increase with aging of the hops. Therefore, if a brewer wishes to maximize the hoppiness potential from these hop varieties, they should be "mildly aged" before brewing.

Category IV hop varieties have a relatively low total hoppiness potential when fresh that remains low when the hops are aged. These hops are Nugget, Cluster, Perle, Columbia, and Olympic. The reason these hops are low in hoppiness, both fresh and aged, is that they all are "good keepers" with high α-acids levels. In other words, the total hoppiness potential (sigma) of the aged hops is low because these hops have not oxidized as much as the other varieties

TABLE IX
Categorization of the Total Hoppiness Potential or Sigma for 20 Hop Varieties, Before and After Aging, Based on a Model Brew Wort

	Sigma (μl/kg wort)			
	Fresh		Aged	
	Low	High	Low	High
Category I				
Kirin II		20.12		22.00
Wye Challenger		10.05		12.14
Wye Target		7.29		7.79
Avg. Σ^{TOT}_{HP}		12.49		13.98
Category II				
Cascade		10.05	3.91	
Galena		7.92	6.41	
Brewer's Gold		5.75	5.64	
Avg. Σ^{TOT}_{HP}		7.91	5.32	
Category III				
Hersbrucker	4.50			13.17
Tettnang	5.44			10.90
Record	4.11			9.80
Fuggle	6.58			9.75
Blisk	3.02			8.80
Eroica	6.15			8.10
Hallertau M. F.	3.38			6.50
Willamette	4.29			6.25
Styrian	3.69			5.99
Avg. Σ^{TOT}_{HP}	4.57			8.81
Category IV				
Nugget	3.87		5.30	
Cluster	3.13		5.19	
Perle	3.12		3.92	
Columbia	2.25		3.47	
Olympic	2.69		3.22	
Avg. Σ^{TOT}_{HP}	3.01		4.22	

under the same storage conditions. Because these hops are good keepers and have high α-acids levels, they are generally considered "bitter" hops, which are traditionally used for their bittering potential and not necessarily for their hoppiness potential.

It is interesting to note that Perle hops have fallen into this bitter hop category IV. Perle is considered an aroma-type hop and has a very high level of α-humulene in the hop oil. However, because Perle does not oxidize as rapidly as other aroma-type hops, it does not increase in the oxidation products hoppiness potential group (Σ_{HP}^{OxP}) with age. This indicates that for a hop variety to be considered an aroma type, it must possess two attributes: it must be high in α-humulene, and it must oxidize at a fairly steady rate in order to increase its hoppiness potential (sigma).

SUMMARY

Evaluation of 20 different hop varieties, under fresh and aged conditions, showed losses of α-acids, hop oil (ml/100 g hops), and myrcene (μl/g α_o) in all varieties. The amount of loss of the α-acids, hop oil, and myrcene appears to be related to the amount of myrcene that is initially present in the fresh hop oil. In addition, 24 other compounds commonly found in hop oil were identified, quantified, and standardized to an original α-acids basis. The compounds were grouped according to their suspected hoppy-flavor contribution to final beer. The groups were oxidation products ("noble" hop aroma), floral compounds, and citrus compounds.

A significant positive correlation was found between the amount of α-humulene in hop oil and the amount of oxidation products of α-humulene in the aged hop oil samples. Significant correlations were found for both the floral compound group and citrus compound group between fresh and aged hops. Hop varieties that were high in floral compounds and citrus compounds when fresh remained high in these flavor groups when aged.

Based on a model brewery calculation, these 20 hop varieties, both fresh and aged, were standardized to an equal original α-acids hopping rate. The resulting hoppiness potential contribution of each of the flavor groups (Σ_{HP}^{OxP}, Σ_{HP}^{F}, and Σ_{HP}^{C}) and the total hoppiness potential (Σ_{HP}^{TOT}) of all three groups were evaluated for all 20 varieties. From this exercise, four categories of hop types became apparent (Fig. 14). Category I hops had a high hoppiness potential when fresh and retained this high hoppiness potential when aged; these hops are Kirin II, Wye Challenger, and Wye Target. Category II hop varieties were high in hoppiness potential when fresh but lost their hoppiness contribution after aging; these were Cascade, Galena, and Brewer's Gold. Category III consists of Hersbrucker, Tettnang, Record, Fuggle, Blisk, Eroica, Hallertau M. F., Willamette, and Styrian hop varieties. These hop varieties showed an increase in total hoppiness potential (sigma) after aging, which indicates that a certain period of aging should increase the hoppiness potential from these varieties. Category IV includes hops with low hoppiness potential when fresh and low hoppiness potential after aging. The varieties in this category are Nugget, Cluster, Perle, Columbia, and Olympic. These hops are "good keepers," and this lack of oxidation prevents them from being aroma hops. Hop varieties in category IV are considered bitter hops, with the exception of Perle.

With existing gas chromatographic and spectrophotometric methods, a brewer is able to analyze and rank hops according to their hoppiness aroma and flavor potential (sigma) along with their bittering potential (α- and β-acids).

ACKNOWLEDGMENTS

We thank S. T. Likens, D. Davidson, P. Lam, L. Rigby, and M. Deinzer for their reviews and comments to this paper. In addition, we thank Patrick Lam, Oregon State University, for his technical advice and analytical support. Finally, we wish to thank the Adolph Coors Company and acknowledge the technical support of the Hop Research Council to G. Nickerson for her work on the project.

LITERATURE CITED

1. American Society of Brewing Chemists. Methods of Analysis, 7th ed. Hops-4. The Society: St. Paul, MN, 1976.
2. American Society of Brewing Chemists. Methods of Analysis, 7th ed. Hops-6. The Society: St. Paul, MN, 1976.
3. Burgess, A. H., and Tatchell, A. R. Page 21 in: Wye College Department of Hop Research for 1950. 1950.
4. DeMets, M., and Verzele, M. *J. Inst. Brew.* 74:74, 1968.
5. Dieckmann, R. H., and Palamand, S. R. *J. Agric. Food Chem.* 22(3):498, 1974.
6. Foster, R. T., II, Weber, K., and Jangaard, N. O. *Tech. Q. Master Brew. Assoc. Am.* 18(3):109, 1981.
7. Hartley, R. D. *J. Inst. Brew.* 73:6, 1967.
8. Hashimoto, N. *Rept. Res. Lab. Kirin Brewery Co.* 13:1, 1970.
9. Hautke, P. *Brauwissenschaft* 29(10):311, 1976.
10. Hop Research Annual Report, Oregon State University, p. 147, 1979.
11. Kuroiwa, Y., Kokubo, E., and Hashimoto, N. *Tech. Q. Master Brew. Assoc. Am.* 10(4):215, 1973.
12. Likens, S. T., Nickerson, G. B., and Zimmerman, C. E. *Am. Soc. Brew. Chem., Proc. 1970*, p. 68.
13. Narziss, L. *Brauwelt 23:834*, 1978.
14. Peacock, E. V., and Deinzer, L. M. *ACS. Symp. Ser.* 170:119, 1981.
15. Peacock, E. V., and Deinzer, L. M. *J. Am. Soc. Brew. Chem.* 39(4):136, 1981.
16. Peacock, E. V., Deinzer, L. M., Likens, S. T., Nickerson, G. B., and McGill, L. A. *J. Agric. Food Chem.* 29:1265, 1981.
17. Peacock, E. V., Deinzer, L. M., McGill, L. A., Wrolstad, R. E. *J. Agric. Food Chem.* 28:774, 1980.
18. Pickett, J. A., and Sharpe, F. R. *J. Inst. Brew.* 82:333, 1976.
19. Rehberger, A. J., and Bradee, L. H. *Tech. Q. Master Brew. Assoc. Am.* 12(1):1, 1975.
20. Roberts, J. B. *J. Inst. Brew.*, 69:343, 1963.
21. Sharpe, F. R., and Laws, D. R. J. *J. Inst. Brew.* 87:96, 1981.
22. Shimazu, T., Hashimoto, N., and Kuroiwa, Y. *Rept. Res. Lab. Kirin Brewery Co.* 17:15, 1974.
23. Snedecor, G. W., Cochran, W. G. Statistical Methods. 6th ed. The Iowa State University Press: Ames, IA, 1967.
24. Tressel, R., Friese, L., Fendesack, F., Koppler, H. *J. Agric. Food Chem.* 26:1426, 1978.
25. Whitear, A. L. *J. Inst. Brew.* 72:177, 1966.
26. Wright, R. G., and Connery, F. E. *Am. Soc. Brew. Chem., Proc. 1951*, p. 87.

[Received July 8, 1985]