The Development of Brewing Quality Characteristics in Hops During Maturation

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ABSTRACT

The relative concentrations of hop constituents important to brewing are dependent upon the hop variety and maturation stage at time of hop harvest. For the hop grower, maximum dry matter content at harvest generally will result in higher yield (lb/ac). However, maximum dry matter content will not necessarily result in hops with maximum brewing quality characteristics.

Four hop varieties (Galena, Nugget, Mt. Hood and Willamette) were harvested at weekly intervals over a six-week period from crops 90, 91, 92 and analyzed for brewing quality using standard methods of analyses. For all four varieties, the alpha-acids concentration peaked at 22-24% dry matter while the beta-acids concentration peaked at less than 22% dry matter. The total essential oil fraction continued to increase in all varieties well beyond normal harvest dates. This increase in essential oil is primarily due to the synthesis of myrcene. The H/C ratio remained relatively constant as the total oil increased.

Certain industry recognized varietal characteristics remained constant over the maturation period while others significantly changed. It may be possible to adjust harvest timing in an attempt to maximize certain brewing quality characteristics.

INTRODUCTION

The relative concentration of hop constituents important to brewing are dependent upon the hop variety and maturation stage at time of hop harvest. In 1939 Rabak(19) reported that in the commercial growing of hops, careful consideration to the proper time of picking is required to produce hops of highest brewing quality. From data collected in crop years 1935 through 1938 on the Cluster variety, Rabak(19) concluded that the stage at which hops are prime in quality extends over a period of approximately four weeks. From the hop growers’ viewpoint, earlier picking would result in economic losses due to increased costs of picking and drying and lower yield (lb/ac).

Over the past 40 to 50 years, optimal harvest date has been primarily predicted by analyzing cone samples for maximum soft resin or maximum alpha-acids content(10,11,19). More recently, the dry-matter content of green cone samples has also been used to predict hop maturity. These practices do not necessarily result in hops with the optimum blend of brewing quality characteristics desired by brewers.

The major brewing quality characteristics of importance to brewers consist of the alpha-acids, beta-acids, co-humulone as a percentage of the alpha-acids, the alpha-acids/beta-acids ratio, total essential oil, the essential oil components and relative concentrations, and storage stability. These parameters are also of utility in the determination of varietal definition(16,17).

In 1956 Howard, et al(11) showed that in the hop varieties Brewers Gold and Northern Brewer, the proportions of co-humulone in the alpha-acids and co-lupulone in the beta-acids are lower in the early stages of ripening, then increase concurrently to those characteristic of the variety sometime before optimum maturity. It has also been reported that beta-acids synthesis is greater during early stages of maturity and that alpha-acids synthesis is greater during later stages of maturity(2,12,14), as a consequence, alpha-acids/beta-acids ratios would be lower in
the early stages of maturity than those characteristic of the variety.

In contrast to Howard, et al. Maier(15) reported that the proportions of co-humulone are relatively stable in six German grown varieties during the period of ripening.

In addition to the alpha-acids and beta-acids, the total essential oil, the essential oil composition and storage stability are considered when assessing hop quality. There are limited data in the literature on the variability of these characteristics during the ripening stages of hops.

A hop maturity study was initiated in 1989 to help establish a better understanding of when to harvest specific varieties of hops for maximum brewing value and to determine the variability of varietal characteristics during the ripening stages of commercially grown hops.

**EXPERIMENTAL**

Willamette, Mt. Hood, Nugget and Galena hops from the 1990, 1991 and 1992 crop years were obtained from the John I. Haas, Inc., Yakima Golding Farm located South of Toppenish, Washington.

At approximately 28 days prior to normal commercial harvest dates, one randomly selected side-arm was removed from 75 hop plants (3 replicates of 25 plants each). The hop cones were hand harvested and composited for laboratory analyses. Sampling was conducted at 7 day intervals until approximately 14 days beyond normal commercial harvest dates. The analytical data for each variety were averaged over the three replicates for each sample date.

**Chemical Analyses**

From each composite sample of green hops, a subsample was removed for dry matter determination and the remainder of the sample was dried in a laboratory dryer operating at about 57°C (135°F) to 8% moisture for chemical analysis.

**Dry Matter.** The dry matter content of green hops was determined using the American Society of Brewing Chemists (ASBC) distillation method (HOPS-4 A)(1), with trimethyl pentane.

**Moisture.** The moisture content of the dried hop samples was determined by the ASBC air oven method (HOPS-4 A)(1) using a Perkin Elmer Lambda 4A spectrophotometer (Perkin Elmer Corp., Norwalk, Connecticut). The co-humulone proportion of the alpha-acids and co-lupulone proportion of the beta-acids were determined using High Performance Liquid Chromatography (HOPS-4 A)(1) performed on a Hewlett Packard 1090 liquid chromatograph (Hewlett-Packard Company, Fullerton, California) equipped with a filter photometer operating at 313 nm and an HP 3392A electronic integrator. The analytical column was a 250 x 4.6 mm Nucleosil C18, 5 micron manufactured by Alltech Associates, Inc., (Deerfield, Illinois).

The Hop Storage Index (HSI) was determined using spectrophotometric analysis of the ASBC(1).

**Essential Oil.** The total essential oil was determined using the steam distillation method of the ASBC (HOPS-13)(1). The proportions of myrcene, humulene and Caryophyllene components is the essential oil were determined using the gas chromatographic method described by Nickerson, et al(9) on a Hewlett Packard 5890A gas chromatograph equipped with a HP 7673A auto injector, flame ionization detector and a HP 3393A electronic integrator. The analytical column was a fused silica capillary 60 M x 0.32 mm Durawax-4 manufactured by J & W Scientific, Inc., (Rancho Cordova, California).

**Six Month Storage Index.** Storage stability of the hop samples was determined after storing dried cone samples in the dark for 6 months at a temperature of 22°C (72°F). The percent transformation was calculated according to the method described by Likens, et al(14,18).

**RESULTS AND DISCUSSION**

The hop maturity study follows the development of chemical components important in the brewing process during the various stages of ripening. Since the early 1970s, several new hop varieties have been released by hop breeding programs for commercial hop production. It is apparent that this trend will continue well into the future; therefore, a more thorough understanding of the genetic variance between hop varieties as related to brewing quality and varietal definition is evident.

Data were collected over a three-year period from four commercially grown hop varieties, two of which are classified as "bitter" hops and two classified as "aroma" hops. The bitter varieties studied were 1) Galena: released for commercial production in 1978 by Romanko, et al(20), bred from open pollination of the Brewers Gold variety, and 2) Nugget: released for commercial production in 1983 by Haunold, et al(6), 5/8 of Nugget's genetic composition is also from the Brewers Gold variety. The aroma varieties studied were 1) Willamette: released for commercial production in 1976 by Haunold, et al(5), a triploid hop bred from a tetraploid Fuggle, and 2) Mt. Hood: released for commercial production in 1989 by Haunold, et al(7), a triploid hop bred from a tetraploid Hallertauer. Approximately 55% of the total U.S. commercial hop acreage in 1992 was composed of these four varieties.

The data from crop years 1990, 1991 and 1992 were averaged over the three-year period to minimize variance in the quality characteristics due to crop year, climatic conditions, fertilization practices, etc. The data from all four hop varieties in the study are shown in Table 1.

**Effect of Harvest Date on Physical Quality Components**

At three weeks prior to harvest all four varieties were at about 18.5% dry matter. The dry matter steadily increased to about 24.5% at two weeks beyond normal commercial harvest dates in the Nugget, Galena and Mt. Hood varieties. The Willamette hops only reached 23.7% dry matter at two weeks post commercial harvest (Figure 1). The Mt. Hood hops were at 24.5% dry matter at one week beyond commercial harvest (Figure 2). All four varieties were commercially harvested at about 23% dry matter.
FIGURE 1.
Dry Matter concentration of Willamette hops during maturation

FIGURE 2.
Dry Matter concentration of Mt. Hood hops during maturation
FIGURE 3.

FIGURE 4.
**FIGURE 5.**

Alpha-acids/beta-acids ratio of Mt. Hood, Nugget, Galena, Willamette hops during maturation.

**FIGURE 8.**

Galena co-humulone and co-lupulone concentrations during maturation. Concentrations are expressed as a percentage of the total alpha-acids and beta-acids respectively.
**FIGURE 7**
Nugget co-humulone and co-lupulone concentrations during maturation. Concentrations are expressed as a percentage of the total alpha-acids and beta-acids respectively.

**FIGURE 8.**
Total essential oil concentration in Willamette hops during maturation, expressed on a dry matter basis.
FIGURE 9.
Total essential oil concentration in Mt. Hood hops during maturation, expressed on a dry matter basis.

FIGURE 10.
Mt. Hood myrcene concentration and humulene/caryophyllene (H/C) ratio during maturation. Myrcene is expressed as a percentage of the total oil.
FIGURE 11.
Alpha-acids concentration after six months storage at 22°C for Mt. Hood, Nugget, Galena and Willamette hops picked at various maturity stages.

FIGURE 12.
Relationship of myrcene concentration in fresh hops to alpha-acids stability for Galena, Mt. Hood, Nugget and Willamette.
For a hop variety that typically produces 2000 Iblacre, such as would be lower than that which is characteristic (2.9 in all four hop varieties. In the Galena hops, the total alpha-acids from 21 days prior to commercial harvest to 14 days post harvest hops with maximum dry matter provided that brewing quality is 9% increase in dry matter would result in an increase will expect a perce 4 5 a percentage of the total oil content-2 Alpha-acids % Total Oil (%) 3 Myrcene (%) 3 Caryophyllene (%) 3 Humulene (%) 3 H/C Ratio 4 6 Mth. Humulone (%) 6 Co-humulone (%) 6 1 Negative numbers are days pre commercial harvest, positive numbers are days post commercial harvest 2 Alpha-acids/beta-acids ratio 3 Expressed as a percentage of the total oil content 4 Humulene/caryophyllene ratio 5 Percent remaining alpha-acids after six months storage at 22°C 6 Expressed as a percentage of the total alpha-acids and beta-acids respectively From the hop grower’s viewpoint, it is desirable to harvest hops with maximum dry matter provided that brewing quality is not sacrificed. For example, a 2% increase in dry matter from 21.5% to 23.5% results in a 9% increase in production (lb/acre). For a hop variety that typically produces 2000 lb/acre, such as Nugget, a 9% increase in dry matter would result in an increase of 1 bale per acre (2000 lb/acre x 1.09 = 2180 lb/acre).

The total beta-acids concentration was relatively constant from 21 days prior to commercial harvest to 14 days post harvest in all four hop varieties. In the Galena hops, the total alpha-acids concentration was also relatively constant throughout the sampling period, remaining at 14 to 16% (Figure 3). Therefore, in the Galena variety, the alpha-acids to beta-acids ratio did not vary during maturation.

At 26 days prior to commercial harvest, the Nugget hops were at 9% alpha-acids while the beta-acids concentration was already at or near maximum (Figure 4). Consequently, the alpha-acids to beta-acids ratio of the Nugget variety harvested prematurely would be lower than that which is characteristic (2.9 - 3.0). The alpha-acids concentration in the Nugget variety peaked at 15%, 5 days prior to commercial harvest at a dry matter content of 22%.

At approximately 10 days prior to harvest, the alpha-acids to beta-acids ratio for all four varieties in the study reached those which are characteristic for the variety (Figure 5). Prior to that, the ratios were lower than the definitive level (except for the Galena hops). For up to 10 days after commercial harvest, the ratios remain characteristic.

The co-humulone and co-lupulone concentrations, expressed as a percentage of the total alpha-acids and total beta-acids respectively, are considered varietal specific characteristics. The co-humulone and co-lupulone concentrations of Galena hops varied slightly throughout the sampling period (Figure 6). The co-humulone ranged from 36.4% early in maturity to 38.4% at late maturity and was 37.7% at commercial harvest. The co-lupulone ranged from 63.8% early in maturity to 64.6% late in maturity and was 64.5% at commercial harvest.

The other three hop varieties in the study, Nugget, Willamette...
and Mt. Hood, varied significantly in co-humulone and co-lupulone concentrations depending on stage of maturity. To illustrate, in the Nugget variety at 26 days prior to commercial harvest the co-humulone was 20.2% and the co-lupulone 43.2% (Figure 7). It was not until the fourth sample date, at 5 days prior to commercial harvest, that the co-humulone and co-lupulone levels reached those characteristic of the Nugget variety, 23.7% co-humulone and 49.9% co-lupulone. Thereafter, the relative proportions of these two characteristics remained relatively constant up to nine days post commercial harvest. Willamette and Mt. Hood hops followed similar patterns.

Therefore, immature to slightly immature commercial hops of these three varieties would tend to have low co-humulone and low co-lupulone values. These data support the work of Harvard, et al(11), where they showed that in the Brewers Gold and Northern Brewer hop varieties the proportions of co-humulone and co-lupulone are low in the early stages of ripening, then increase concurrently to those characteristics of the variety slightly before optimum maturity.

Effect of Harvest Date on Aroma Characteristics

Total essential oil in hops is considered a brewing quality characteristic as well as a varietal characteristic. In general, all four varieties in the study had low essential oil content in the early stages of maturity. The Willamette variety reached a maximum total oil content of about 1.5 ml/100 g hops at or near normal commercial harvest (Figure 8).

In the Mt. Hood hops the total essential oil content continued to increase throughout the sampling period up to about 14 days post commercial harvest when the total oil content was 3.2 ml/100 g hops (Figure 9). By slightly delaying commercial harvest, total essential oil content could be maximized. As a varietal characteristic, total oil content would not be reliable since the characteristic is dependent on stage of maturity when harvested.

The majority of the increase in total oil was due to the myrcene component, which increased from 3% to 49% of the Mt. Hood total oil from early to late maturity (Figure 10). The relative proportions of the oil components humulene and caryophyllene remained stable throughout the sampling period, ranging from a humulene/caryophyllene ratio of 2.3 to 1.9 with one exception, the earliest sample at 28 days prior to commercial harvest the H/C ratio was 2.6 (Figure 10). Hence, the H/C ratio is an excellent characteristic for varietal characterization. These observations were similar for all four varieties in the study and are consistent with the findings of Likens13 work in the early 1960s on the hop varieties, Bullion, Fuggle and Late Cluster.

Effect of Harvest Date on Storage Stability

The stability of the soft resins of hops, particularly the stability of the alpha-acids to oxidation is of value to both the brewer and the hop grower. Storage stability is a characteristic which is variety specific(8,14,18) and in general, the “bitter” varieties of hops exhibit higher degrees of stability than the “aroma” varieties.

The Galena and Nugget hops which were stored at room temperature in the dark for six months lost very little alpha-acids regardless of the maturity stage when picked (Figure 11). However, the aroma varieties, Willamette and Mt. Hood, show a very different trend, which is most pronounced in the Mt. Hood hops (Figure 11).

When Mt. Hood hops were harvested at about 28 days prior to normal commercial harvest the amount of alpha-acids remaining after six months was 84%. Thereafter, this value decreases with each seven day sampling interval to a minimum of 50% remaining, near normal commercial harvest, then for some reason increased on the last two sample dates. At two weeks post commercial harvest the amount of alpha-acids remaining had increased to 59% (Table 1).

It has been stated in the literature3,4 that myrcene may have a role in the oxidation of alpha-acids during hop storage, specifically, as the concentration of myrcene in the fresh hops increases, the Hop Storage Index (HSI) increases. The HSI has been shown to be logarithmically related to the oxidation of hop acids14.

In Figure 12 the percent remaining alpha-acids has been plotted against percent myrcene in the fresh hops for all four varieties in the study. These data do not support the conclusion that myrcene concentration in fresh hops is correlated to oxidation of alpha-acids during storage. Therefore, other factors are involved in the storage stability of hops and further work will be required to identify these factors.

SUMMARY

In all four hop varieties in the study, Galena, Nugget, Willamette and Mt. Hood, the alpha-acids concentration peaks at 22-24% dry matter. Total essential oil continues to increase well beyond normal commercial harvest dates in all four varieties. The humulene/caryophyllene ratios remain constant as total oil increases in all four varieties. In Mt. Hood and Willamette hops, the harvest date is correlated to alpha-acids degradation. It may be possible to determine optimal harvest times for certain hop varieties to maximize specific brewing characteristics.

SUGGESTIONS FOR FURTHER WORK

Identify factors in aroma hops which promote alpha-acids oxidation.

Identify factors in bittering hops which prevent alpha-acids oxidation.

QUESTIONS AND ANSWERS

Q. I noticed that the percents of alpha-acids appeared to be much higher than what we normally see in the commercial crop. Could you explain this?

A. The alpha-acids and beta-acids concentrations have been presented here on a dry matter basis. The commercial crop is reported on an as is basis, which is typically 7-10% moisture. For example: 15% alpha-acids on a dry matter basis is equivalent to 13.5% alpha-acids on an as is basis with 10% moisture content.

Q. In your tests on the stability of stored hops, what temperature were they stored at?

A. Whole hop cones at about 7% moisture were stored in paper bags in the dark at room temperature, 22°C (72°F).
Q. What temperature do you recommend a microbrewery store aroma hops at?
A. For maximum alpha-acids preservation, baled and pelleted aroma hops should be stored at approximately -2°C to 3°C. On the other hand, a certain amount of oxidation of the aroma components may be desirable to individual brewers and as the storage temperature increases the rate of oxidation also increases. Therefore, any recommendations should be made only after considering your entire hopping regime.

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LITERATURE CITED