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Hidden Secrets of the New England IPA

John Paul Maye and Robert Smith

S.S. Steiner, Inc., New York, NY 10065

ABSTRACT

New England India Pale Ale (NEIPA), also known as hazy IPA or juicy IPA, is a relatively new beer style being brewed by craft breweries across the United States. These beers typically have massive hop aroma and flavor yet are not perceived as being very bitter. They can be incredibly hazy, and many impart fruity and juicy flavors. Twelve NEIPAs were analyzed by high-performance liquid chromatography for various hop compounds, and several tests were conducted on the haze itself to determine what it is and is not. Experiments conducted on these beers exposed the hidden secrets of NEIPA. The results indicated that the vast majority of the haze is polyphenol-protein haze and that the haze can act as a carrier to more of the nonpolar hop compounds than are typically found in West Coast style IPA.

Keywords: New England IPA, NEIPA, Juicy, Hazy, Dry hopping

In 2003, John Kimmich started the Alchemist Pub & Brewery in Waterbury, VT, and created a beer called Heady Topper. This hazy, hoppy beer was so unique people thought it deserved its own category, Vermont India Pale Ale (IPA). It was not long before other craft brewers in New England started making their own versions of this beer style, hence the New England style IPA (NEIPA) was born. The grain bill and how the hops are used are different from a typical West Coast style IPA (WC IPA), which tends to have higher clarity and higher bitterness. NEIPA brewers typically use 10–50% high-protein adjuncts such as oats and/or wheat, which contain ~16 and ~13% protein, respectively. About 10% of the oat protein and about 80% of the wheat protein are made up of haze-active proteins called prolamins. Prolamins are proline-rich proteins that can hydrogen bond with polyphenols (from barley and hops) to form common beer haze (11–13). Little to no hops are added to the kettle during the boil, but instead about one-third to one-half of the hop dosage is added to the whirlpool, typically after the whirlpool temperatures are lowered to ~180°F or less, to retain as much of the hop oil as possible and minimize α-acid isomerization. Dry hopping is also performed a little differently, in that the hops are typically added to the fermenter 24 to 48 h after the yeast is pitched, usually at a dose rate of at least 1 lb/barrel per day for at least 3 to 4 days if not more. Hop addition to the fermenter allows the yeast to biotransform oxygenated hop oils such as geraniol and linalool into fruity and floral aroma compounds such as geraniol acetate, citronellol, citronellol acetate, and α-terpineol, to name a few (5,15), although the scope of these transformations is dependent on yeast strain and hop variety. Many craft brewers believe the addition of at least 3 lbs of hops per barrel, to the fermenter, of geraniol-rich hop varieties such as Bravo, Cascade, and Centennial, to name a few (15), is required to obtain the signature fruity, juicy flavors of the style.

Dry hopping is known to change the hop acid composition of beer (9,10), and this lab has a large database for WC IPA but not NEIPA. High-performance liquid chromatography (HPLC) analysis of several hop compounds in 12 NEIPAs was compared with those of WC IPA. In addition, turbidity tests were conducted on the beers, and several tests were conducted on the haze itself to better understand its composition and any unexpected properties.

Materials and Methods

Beer samples measuring ~140 g were brought to room temperature and treated with one drop of octanol and degassed by bath sonication. These beer samples were analyzed by HPLC using the American Society of Brewing Chemists (ASBC) method Beer-23E (2). A C18 HPLC column (2.7 µm, 4.6 × 50 mm, Raptor column, Restek) was used with a mobile phase of 72.5% methanol/26.5% water/0.85% phosphoric acid/0.075 mM Na_2EDTA. Concentrations of iso-α-acids were determined using the HPLC calibration standard ICS-I3, which was purchased from ASBC. α-Acids and β-acids were determined at 270 nm using the HPLC calibration standard ICE-3, purchased from ASBC. A humulinone-dicyclohexylamine HPLC calibration standard (8) was produced in-house and used to calibrate the HPLC for humulinone (oxidized α-acid) analysis. Xanthohumol was calibrated at 367 nm using the new calibration standard ICS-X1 (96.0% xanthohumol; obtained from ASBC). Myrcene, a monoterpene with a conjugated diene, has a strong absorbance at 222 nm. The HPLC was calibrated at 222 nm using myrcene from Aldrich Chemical Co. (analytical standard 64643). Myrcene eluted from a C18 column between the iso-α-acids and the α-acid cohumulone.

Turbidity measurements of the NEIPAs (brought to room temperature and degassed via bath sonication) were made using a VWR Scientific model 34100-787 turbidity meter. For beer samples with turbidity >200 NTU, samples were diluted with reverse osmosis (RO) water, and the turbidity measurement was multiplied by the dilution factor. A 1,000 NTU turbidity standard (formazin standard from Aldrich Chemical Co.) was diluted with RO water to calibrate the turbidity meter; the calibration curve required a second-order polynomial fit.

Some degassed beer samples were centrifuged in 50 mL centrifuge tubes using a VWR Scientific centrifuge at 1,900 rpm for 10 min. The supernatant was reanalyzed for turbidity and hop compounds by HPLC.

E-mail: jmaye@hopsteiner.com

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Sediment from 12 cans of seven different NEIPAs (stored for 2–5 months) was obtained via centrifuge, totaling 8.2 g. This sediment was further washed with 16.4 g of water and centrifuged; 4.32 g of the sediment was freeze dried, and 0.89 g of dry solids were obtained. This freeze-dried sediment was analyzed by HPLC for hop compounds, and the polyphenol content was determined using ASBC method Beer-35 (3). The protein content (from Kjeldahl nitrogen) was determined by Galbraith Laboratories. The carbohydrate concentration of the freeze-dried sediment was determined by acid digestion to simple sugars (6) and spectral analysis at 490 nm using glucose as the standard (4). Fatty acid content of the freeze-dried sediment was determined by saponification. The sediment (104 mg) was digested for 1 h at 70°C with 37 mg of 45% KOH and 640 mg of water. The saponified sample was brought to 10 mL with isopropyl alcohol and 0.27 g of phosphoric acid. This sample was analyzed by HPLC using the mobile phase of 77% methanol/22% water/0.85% phosphoric acid and the aforementioned HPLC column. Pure linolenic acid, linoleic acid, and oleic acid (obtained from Aldrich Chemical Co.) were used to calibrate the HPLC at 202 nm.

Results and Discussion

HPLC analysis was performed on 12 NEIPAs to measure the concentration of iso-α-acids, humulinones, α-acids, β-acids, xanthohumol, and myrcene. Table 1 lists the range and average concentrations of these compounds and compares them to the average concentrations found in WC IPAs as determined by this laboratory. Table 2 lists the results of these same hop compounds for each of the 12 NEIPA beers. Owing to the way NEIPAs are hopped, it is not surprising that the iso-α-acid concentrations are quite a bit lower than WC IPAs and the humulinone concentrations higher. Humulinones are reported to be 66% as bitter as iso-α-acids (1) and are reported to have a smooth, nonlingering bitterness (9). NEIPAs on average contain 1.3 ppm of humulinones for every 1 ppm of iso-α-acids, which means nearly half the sensory bitterness is coming from humulinone. This helps explain why NEIPAs are not perceived as being as bitter as WC IPAs. Interestingly, higher concentrations of nonpolar hop compounds, such as α-acids, xanthohumol, myrcene, and β-acids, were found in NEIPAs than in WC IPAs. The α-acid concentration ranged from 17 to 72 ppm, with the average being 31 ppm, compared with an average of 13 ppm of α-acids in WC IPA. The xanthohumol concentration ranged from 0.9 to 3.5 ppm, with an average of 2 ppm, versus WC IPA having a maximum solubility of 0.7 ppm of xanthohumol. The myrcene concentration was also higher in NEIPAs, having a range of 0.5–2.5 ppm with an average of 1.4 ppm versus a WC IPA having less than 0.3 ppm. What was totally unexpected was the concentration of β-acids (lupulone) in these beers, which ranged from 1 to 14 ppm with the average being 5 ppm. β-Acids are essentially insoluble in all styles of beer, with the exception of Hefe Weiss beers, for which 0.5 to 1 ppm is typically found. However, Weiss beers are generally bottle conditioned and the β-acids usually come from the yeast, on which they are absorbed. α-Acids have antioxidant properties, primarily owing to their chelation with iron (7,14,16,18), and xanthohumol, another antioxidant, is perhaps the world's most powerful hydroxyl radical scavenger (17,19). High concentrations of these antioxidants in the NEIPAs should improve the flavor and aroma stability of these beers, yet many brewers claim these beers have short shelf lives.

The 12 beers had their haze tested via a turbidity meter, and the haze ranged from 119 to 1,774 NTU with the average being 547 NTU, versus a WC IPA, which typically has less than 30 NTU of haze. NEIPAs are said to use low-flocculent yeast, so the yeast counts of six beers were measured and compared with their haze (Table 3). Yeast counts of 1 and 5 million yeast cells/mL were prepared, and their turbidity measured only 10.5 and 68.0 NTU, respectively. Given that most of the beers contained less than 1 million yeast cells/mL, this means that yeast was not even a minor contributor to haze. Only one beer, J, had yeast

Table 1. HPLC analysis, New England IPAs (NEIPAs) versus West Coast IPAs

Hop compound	NEIPA range (ppm)	NEIPA average (ppm)	West Coast IPA average (ppm)
Iso-α-acids	5–32	20	48
Humulinone	12–38	26	11
α-Acids	17–72	31	13
β-Acids	1–14	5	0
Xanthohumol	0.9–3.5	2	0.7
Myrcene	0.5–2.5	1.3	<0.3

Table 3. Yeast contribution to turbidity of New England IPAs

Beer	Initial turbidity (NTU)	Yeast count (million cells/mL)	Contribution of yeast to turbidity
B	1,328	<1	<1%
E	410	0.1–0.2	<1%
F	299	0.2	<1%
H	224	<1	<4%
J	147	5	29%
L	119	0.2	<2%

Table 2. Detailed HPLC analyses of hop compounds (mg/L) of all 12 New England IPA beers and turbidity

Beer	Humulinones	Iso-α-acid	α-Acids	Myrcene	Xanthohumol	β-Acids	Turbidity (NTU)
A	34.6	18.2	31.8	1.2	3.5	9.1	1,774
B	37.9	26.7	72.1	2.5	3.0	8.3	1,328
C	38.4	11.4	48	2.4	3.1	14	1,071
D	23.5	21.3	31.8	2.3	2.1	5.6	654
E	12	20	32.2	1.7	2.0	5.4	410
F	34.5	31.7	34.4	1.7	1.5	4.3	299
G	16.2	22.8	17.2	0.6	1.7	1.3	226
H	19.6	21.8	27.7	1.3	1.3	3.6	224
I	25.4	16.9	20.7	0.5	1.8	2.3	173
J	25.5	5.5	23.1	0.7	1.0	1.9	147
K	16	16.5	16.9	0.6	2.0	1.3	137
L	28.4	29.5	17.6	0.6	1.1	1.3	119
Average	26	20	31	1.3	2.0	4.9	547

counts high enough for it to significantly contribute to the haze measurement (at 29% of the total), and this was owing to the relatively low turbidity of that beer, 147 NTU.

Given the elevated concentration of nonpolar hop compounds found in NEIPA, some beers were spiked with xanthohumol, α-acids, and β-acids to see what their contribution to haze could be (Fig. 1). As the data show, xanthohumol and α-acids contribute little to haze, whereas low concentrations of β-acids can. However, the combined amount of hop acids contributes less than 10% at most of the total haze in NEIPAs. To see if there was a relationship between the solubility of nonpolar hop compounds and haze, the concentrations of myrcene, xanthohumol, and β-acid in NEIPA beers were plotted against their turbidity (Fig. 2). Figure 2 shows nearly a linear correlation between the myrcene concentration and xanthohumol concentration versus haze. Although there was not a linear correlation between haze and β-acid concentration, generally more haze equals more β-acids.

To see if the haze might be acting like a carrier or emulsifier, two NEIPA beers had their hop compounds measured before and after the beers were centrifuged (Table 4). Centrifugation of beer 1 reduced the haze from 1,071 to 295 NTU and beer 2 from 1,774 to 889 NTU. Interestingly, centrifugation removed little of the beer soluble (polar) hop compounds humulinone and iso-α-acid. However, it did significantly reduce the concentrations of the nonpolar hop compounds: α-acids, β-acids, xanthohumol, and myrcene. Centrifuging beer 1 reduced the haze by about 70% and the concentration of α-acids by 46%, xanthohumol by 52%, myrcene by 54%, and β-acids by 85%. Centrifuging beer 2 reduced the haze by 50% and the concentration of α-acids by 32%, xan-

Figure 1. Effect of hop compounds on turbidity of a West Coast IPA. Xn = xanthohumol.

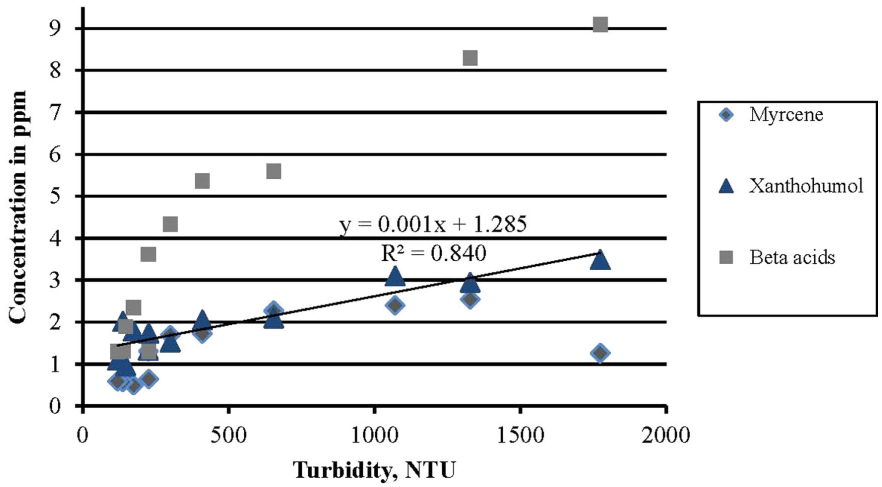

Figure 2. Concentration of hop compounds versus haze of New England IPAs.

Table 4. Hop compound concentration in New England IPA before and after centrifuging (1,900 rpm for 10 min)[a]

Beer	Turbidity (NTU)	Humulinone (ppm)	Iso-α-acids (ppm)	α-Acids (ppm)	Myrcene (ppm)	Xanthohumol (ppm)	β-Acids (ppm)
1 H	1,071	38.4	11.4	48	2.4	3.1	14
1 C	295	37.9	10.7	26	1.1	1.5	2
2 H	1,774	34.6	18.2	52	1.26	3.5	9.1
2 C	889	33.8	17.5	35	0.78	2.1	4.3

[a] H = hazy beer before centrifuge; and C = centrifuged beer.

thohumol by 40%, myrcene by 38%, and β-acids by 52%. Thus, the elimination or reduction in haze reduces the concentration of nonpolar hop compounds to concentrations more similar to what one would see in WC IPAs. Therefore, the haze in NEIPAs is acting like a carrier and is responsible for the elevated concentrations of nonpolar hop compounds.

To better understand what the haze is composed of, haze precipitate was isolated from several beers and freeze dried. A sample of the freeze-dried material was sent to Galbraith Laboratories for protein analysis, and additional testing was conducted to measure the concentration of polyphenols, carbohydrates, and fatty acids (Table 5). Analysis showed the haze contains 35.7% protein, 11.1% carbohydrates, 3.4% polyphenols, and 0.9% saponified fatty acid, of which 0.2% is linolenic acid, 0.5% linoleic acid, and 0.2% oleic acid. Given the use of high-protein adjuncts such as oats and wheat, which are rich in the haze-active prolamins, and the abundance of polyphenols coming from malt and hops, it should not be a surprise that the haze is primarily a protein-polyphenol complex, which is well documented in the literature (11–13). The haze was also analyzed for myrcene, α-acids, β-acids, xanthohumol, iso-α-acids, and humulinones (Table 6). Interestingly, given the high solubility of iso-α-acids and humulinones in beer, the freeze-dried haze contained low concentrations of these compounds. The low concentration of myrcene in the freeze-dried sample was most likely owing to its loss upon high-vacuum drying. However, given the high concentration of α-acids in NEIPAs and the poor solubility of β-acids in beer (Table 7), the freeze-dried haze contained 8% α-acids and 3% β-acids. Thus, 63% of the haze composition was accounted for in the aforementioned analyses.

Finally, the haze stability of these beers was measured over 5 months (Fig. 3). In most cases the haze dropped below 300 NTU after 1–2 months, demonstrating a common problem with these beers: haze stability over time.

Summary and Conclusion

Detailed HPLC analysis of 12 NEIPAs showed the average iso-α-acid concentration to be 20 ppm and the average humulinone concentration to be 26 ppm. This means that nearly half the sensory bitterness of these beers comes from the smooth

Table 7. Relative solubility of hop compounds in beer[a]

Common name	Scientific name	Solubility in beer
Iso-α-acids	Isohumulone	++
Oxidized α-acids	Humulinone	+++
α-Acids	Humulone	+
β-Acids	Lupulone	−−−−
Xanthohumol	Xanthohumol	−
Myrcene	β-Myrcene	−−

[a] Soluble (polar): ++++; and insoluble (nonpolar): −−−−.

Table 5. Protein, carbohydrate, polyphenol, and fatty acid composition of freeze-dried haze

Protein	Carbohydrate	Polyphenols	Fatty acids	Linolenic acid	Linoleic acid	Oleic acid
35.7%	11%	3.4%	0.9%	0.2%	0.5%	0.2%

Table 6. Hop compound composition of freeze-dried haze

Sample	Myrcene (mL/100 g)	α-Acids (%)	β-Acids (%)	Xanthohumol (%)	Iso-α-acids (%)	Humulinones (%)
Freeze-dried haze	0.1	8	3	0.4	0.3	0.2

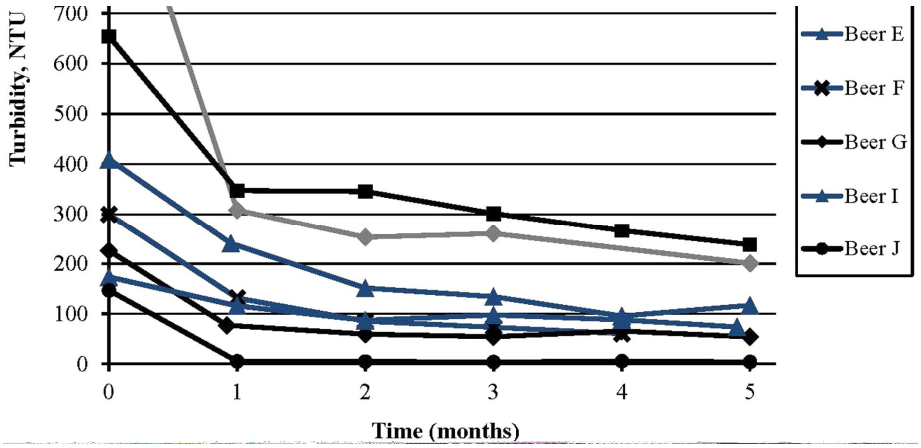

Figure 3. Haze stability of New England IPAs stored at 3°C versus time.