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Full Length Research Paper

Volatile components of aroma hops (*Humulus lupulus* L.) commonly used in beer brewing

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The essential oils from seven different aroma (finishing) varieties of hops (*Humulus lupulus* L.), "Cascade", "Hallertauer", "Northern Brewer", "Saaz", "Sterling", "Vanguard", and "Willamette", were obtained by hydrodistillation and analyzed by gas chromatography – mass spectrometry. A total of 98 compounds were identified with myrcene and α-humulene dominating the profiles. "Cascade" and "Northern Brewer" were rich in monoterpene hydrocarbons, chiefly myrcene, while sesquiterpene hydrocarbons, mostly α-humulene, dominated "Hallertauer", "Saaz", "Sterling", and "Vanguard". "Willamette" had an even distribution of monoterpenes and sesquiterpenes.

Key words: Chemical composition, aroma hops, cascade, Hallertauer, Northern Brewer, Saaz, Sterling, Vanguard, Willamette.

INTRODUCTION

Hops (*Humulus lupulis* L.) are used in beer brewing to impart both its distinct aroma and bitter taste (Kovačevič and Kač, 2002). There are currently many varieties of hops, but they can be divided into bittering hops [that is, those with high bitter acids, humulone, cohumulone, lupulone, and colupulone (Ting and Goldstein, 1996)] and finishing or aroma-giving hops (Hornsey, 1999). Finishing hops are generally added to the wort at the end of the boiling process (last 1-2 min) to provide volatile aroma components to the beer (Papazian, 2003). A review on the chemical constituents of hops can be seen in Stevens (1967).

There has been much interest in the chemical variability and aroma of hop volatiles and a number of studies have focused on chemical profiles of hops (Buttery et al., 1965; Likens and Nickerson, 1967; Kralj et al., 1991; Field et al., 1996; Eri et al., 2000; Steinhaus and Schieberle, 2000; Lermusieau and Collin, 2001; Jirovetz et al., 2006; Tofană et al., 2009) and of hop aroma in beer (Peacock et al., 1980; Peacock et al., 1981; Lam et al., 1986; Lermusieau et al., 2001; Liu et al., 2005; Pinho et al., 2006; Kishimoto, 2008). In this work we present the volatile chemical profiles for seven different aroma (finishing) varieties of hops: "Cascade", "Hallertauer", "Northern Brewer", "Saaz", "Sterling", "Vanguard", and "Willamette".

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MATERIALS AND METHODS

Hops

Whole hops were obtained from MoreBeer!™, Concord, California. The hops were hydrodistilled using a Likens-Nickerson apparatus (Likens and Nickerson, 1964) for four hours with continuous extraction with dichloromethane.

Gas chromatography – Mass spectrometry

A gas chromatographic-mass spectral analysis was performed on the essential oils of the finishing hops using an Agilent 6890 GC with Agilent 5973 mass selective detector (EIMS, electron energy = 70 eV, scan range = 45-400 amu, and scan rate = 3.99 scans/s), and a fused silica capillary column (HP 5ms, 30 m × 0.25 mm) coated with 5% phenyl-polymethylsiloxane (0.25 µm phase thickness). The carrier gas was helium with a flow rate of 1 mL/min, and the injection temperature was 200°C. The oven temperature was programmed to initially hold for 10 min at 40°C, then ramp to 200°C at 3°C/min and finally to 220°C at 2°C/min. The interface temperature was 280°C.

A 1% w/v solution of each sample in dichloromethane CH_2Cl_2 was prepared, and 1 µL was injected using a splitless injection technique. Identification of the oil components was based on their retention indices determined by reference to a homologous series of *n*-alkanes, and by comparison of their mass spectral fragmentation patterns with those reported in the literature (Adams,

2007), and stored on the MS library [NIST database (G1036A revision D.01.00)/ChemStation data system (G1701CA, version C.00.01.080)]. The percentages of each component are reported as raw percentages based on total ion current without standardization. The chemical compositions of the hops oils are summarized in Table 1.

Numerical cluster analysis

The ten hops samples were treated as operational taxonomic units (OTUs). The percentage composition of all essential oil components was used to determine the chemical relationship between the different finishing hops essential oil samples by cluster analysis using the NTSYSpc software, version 2.2 (Rohlf, 2005). Correlation was selected as a measure of similarity, and the unweighted pair-group method with arithmetic average (UPGMA) was used for cluster definition.

RESULTS AND DISCUSSION

Cascade

Cascade hops are a popular American aroma hop that has been characterized as floral, fruity, and particularly citrusy (grapefruit), with little earthy or spicy aroma (Brew365). The essential oil of Cascade was dominated by myrcene (48.9%), which may account for the citrus-like aroma of Cascade hops (Jirovetz et al., 2006; Qiao et al., 2008). Other abundant components were α-humulene, which has been described as citrusy (Sawamura et al., 2006), but also as floral and woody (Sant'Anna et al., 2007), or earthy (Jirovetz et al., 2006); (E)-caryophyllene (5.8%), generally described as herbal, spicy, or woody (Sawamura et al., 2006; Sant'Anna et al., 2007; Sádecká and Polovka, 2008); and (E)-β-farnesene (4.4%). The floral and fruity notes of Cascade are likely due to linalool (1.3%) (Goodner et al., 2006; Sawamura et al., 2006; Sádecká and Polovka, 2008; Qiao et al., 2008) and geranyl esters.

Hallertauer

Hallertauer volatiles were dominated by sesquiterpene hydrocarbons (46.5-50.8%), mostly α-humulene (22.7-28.0%), (*E*)-caryophyllene (7.8-9.0%), and (*E*)-β-farnesene (4.6-5.7%), with lesser amounts of γ-muurolene (1.1-1.7%), δ-cadinene (1.9-2.3%), and γ-cadinene (1.1-1.5%). The monoterpene myrcene was also abundant (21.4-24.8%) as well as the oxygenated sesquiterpenoids caryophyllene oxide (2.2%) and humulene epoxide II (3.9-4.0%). Sesquiterpene hydrocarbons are often characterized as having spicy or woody odors (Jiroventz et al., 2006; Sant'Anna et al., 2007; Sádecká and Polovka, 2008) and Hallertauer hops have been described as earthy, spicy, and "noble" (Brew365).

Northern Brewer

Northern Brewer hops have been characterized as "reminiscent of Hallertauer" with a "woody, piney, earthy, minty, and somewhat rustic" aroma (Brew365). Northern Brewer volatiles were dominated by monoterpene hydrocarbons (54.5%), particularly myrcene (52.4%). Other major components were α-humulene (17.2%) and (*E*)-caryophyllene (6.7%). The chemical profile of Northern Brewer, in this study, was very similar to Cascade, with some notable differences in minor components: Cascade had more esters, particularly geranyl esters, while Northern Brewer had 2.5% 14-hydroxy-(*E*)-caryophyllene, which had been previously found to impart a woody odor to hops (Eyres et al., 2007).

Saaz

Three different samples of Saaz hops were analyzed in this study. Two showed very similar chemical profiles with myrcene (25.3-25.7%) and α-humulene (17.4%) dominating. The other Saaz sample was notable in that myrcene concentration (8.0%) was much reduced. Saaz hops had higher concentrations of aliphatic ketones, aldehydes, and carboxylic acids than the other varieties. Saaz hops are classified as one of the true noble varieties with spicy, cinnamon-like, and earthy qualities.

Sterling

Sterling hops have been characterized as generally spicy and herbal with a little floral aroma (Brew365), and in this study, both α-humulene (41.6%) and myrcene (35.8%) co-dominated the essential oil. Additional notable components were linalool (1.1%), (*E*)-caryophyllene (7.4%), δ-cadinene (1.3%), and humulene epoxide II (2.4%).

Vanguard

The essential oil of Vanguard hops had the highest percentage of sesquiterpene hydrocarbons (70.3%) with α-humulene (51.2%) and (*E*)-caryophyllene (11.3%) predominating, and minor amounts of δ-cadinene (2.4%), γ-cadinene (1.2%), and γ-muurolene (1.1%). The concentration of myrcene was relatively low (16.8%) in this variety compared to others in this study. Vanguard is described as having a noble and mild aroma, evenly herbal, woody, and spicy (Brew365).

Willamette

The aroma of Willamette hops has been described as vegetal or earthy, slightly spicy, fruity, and floral (Brew365). The concentrations of monoterpene hydrocarbons (40.9%), mostly myrcene (39.8%), and sesquiterpene hydrocarbons (47.3%), predominantly α-humulene (32.5%) and (*E*) - caryophyllene (8.8%), is relatively balanced. The other hop varieties in this study were either

Table 1. Chemical compositions of the essential oils of finishing (aroma) hops.

RI[b]	Compound	Percent composition[a]								
		Cascade	Hallertauer		Northern	Saaz			Sterling	Vanguard	Willamette
			#1	#2	Brewer	#1	#2	#3			
749	4-Methyl-2-pentanone	---	---	---	0.1	1.1	3.4	1.1	---	---	---
759	3-Methyl-2-pentanone	---	---	---	---	---	1.0	0.2	---	---	---
774	3-Methyl-2-buten-1-ol	0.1	---	---	---	0.5	0.5	0.4	---	---	---
782	3-Methyl-2-butenal	0.2	---	---	0.3	0.6	0.5	0.5	tr	0.9	tr
799	Hexanal	---	---	---	---	---	0.2	0.1	---	---	---
833	Furfural	---	---	---	---	tr	---	---	---	---	---
840	Isovaleric acid	0.4	---	---	---	1.1	2.7	3.8	---	---	---
850	2-Methylbutanoic acid	---	---	---	---	---	0.5	0.6	---	---	---
854	(2*E*)-Hexenal	---	---	---	---	---	0.1	---	---	---	---
909	Isobutyl isobutyrate	0.2	---	---	0.3	---	---	---	---	---	tr
941	α-Pinene	0.3	---	---	0.2	0.2	0.4	0.4	---	---	---
956	4-Methyl-2-pentenolide	0.1	0.4	0.1	0.5	1.5	1.5	1.5	0.3	0.2	0.2
975	Isoamyl propionate	0.3	---	---	---	---	---	---	---	---	---
978	β-Pinene	1.5	0.4	0.3	1.2	0.6	1.2	1.0	0.6	0.2	0.5
981	1-Octen-3-ol	---	---	---	---	---	0.2	0.2	---	---	---
988	6-Methyl-5-hepten-2-one	---	---	---	---	0.3	0.4	0.4	---	---	---
991	Myrcene	48.9	24.8	21.4	52.4	8.0	25.3	25.7	35.8	16.8	39.8
1014	Isoamyl isobutyrate	0.3	0.7	0.3	1.6	---	---	---	---	---	0.4
1017	Isobutyl isopentanoate	0.8	---	---	---	---	---	---	---	---	---
1025	Methyl heptanoate	0.2	0.5	1.1	0.1	0.6	0.9	0.9	---	0.2	0.1
1028	Limonene/β-Phellandrene	1.1	0.5	---	0.6	0.6	1.2	0.9	0.4	0.2	0.6
1042	Phenylacetaldehyde	---	---	---	---	---	0.1	---	---	---	---
1047	(*E*)-β-Ocimene	0.2	tr	---	0.1	---	0.1	---	tr	---	tr
1053	Prenyl isobutyrate	---	tr	---	---	---	---	---	---	---	---
1069	*cis*-Linalool oxide (furanoid)	---	0.1	0.1	---	---	0.1	0.2	---	---	---
1078	Heptanoic acid	---	---	---	---	---	0.6	0.6	---	---	---
1090	2-Nonanone	---	---	0.3	---	---	0.5	0.4	---	---	---
1092	6,7-Epoxymyrcene	0.2	0.3	---	0.2	---	---	---	0.2	0.1	---
1097	Linalool	1.3	1.9	3.2	1.0	0.8	1.6	1.6	1.1	0.2	1.0
1102	2-Methylbutyl 2-methylbutyrate	---	0.3	0.3	0.2	---	---	---	---	---	0.2
1103	*n*-Nonanal	0.1	---	---	---	0.5	0.5	0.4	---	0.2	---
1107	2-Methylbutyl isovalerate	0.1	0.1	tr	0.1	---	---	---	---	---	---
1127	Methyl octanoate	0.2	0.3	0.3	0.4	---	0.3	0.3	tr	0.2	0.1
1172	Octanoic acid	---	---	---	---	---	0.1	0.1	---	---	---

Table 1. Contd.

1188	α-Terpineol	tr	0.2	0.1	---	---	---	---	---	---	---
1193	2-Decanone	---	0.2	0.2	---	0.5	0.5	0.5	0.5	---	---
1211	Methyl nonenoate	---	---	---	---	0.2	0.3	0.3	---	---	---
1225	Methyl nonanoate	---	0.2	0.1	0.1	0.5	0.4	0.5	---	---	---
1240	Neral	---	tr	tr	---	---	---	---	---	---	---
1247	Heptyl isobutanoate	---	---	tr	---	---	---	---	---	---	---
1254	Geraniol	0.9	0.7	0.4	1.1	tr	0.3	0.3	0.2	---	0.2
1270	Geranial	---	0.2	0.1	tr	---	---	---	---	---	---
1270	Nonanoic acid	---	---	---	---	tr	0.3	0.4	---	---	---
1293	2-Undecanone	0.2	0.6	0.8	0.3	1.6	1.3	1.4	0.2	0.7	0.1
1295	Perilla alcohol	0.1	0.2	0.2	0.1	tr	0.2	0.2	0.1	---	0.1
1307	Methyl (4*Z*)-decenoate	0.8	1.5	1.6	1.3	2.2	1.9	1.9	0.4	0.8	0.4
1312	Unidentified	0.5	1.2	1.5	0.8	1.0	0.9	0.9	---	0.4	0.5
1324	Methyl geranate	0.4	0.7	0.7	---	0.6	0.5	0.5	0.5	---	0.3
1328	Methyl decanoate	---	---	---	1.0	---	---	---	---	0.1	---
1358	9-Decenoic acid	---	---	---	---	0.4	0.4	0.5	---	---	---
1363	Unidentified	---	---	---	---	---	0.7	0.4	---	---	---
1365	Neryl acetate	---	0.1	---	---	---	---	---	---	---	---
1367	Decanoic acid	---	---	---	---	tr	---	---	---	---	---
1371	α-Ylangene	0.1	0.3	0.3	0.1	tr	0.1	tr	0.1	0.1	0.1
1375	α-Copaene	0.3	0.8	0.9	0.3	0.5	0.4	0.4	0.3	0.4	0.3
1386	Geranyl acetate	1.8	1.6	---	---	tr	---	---	---	---	---
1397	2-Dodecanone	---	0.1	0.1	---	0.4	0.3	0.3	---	---	---
1400	Tetradecane	---	---	tr	---	---	---	---	---	---	---
1405	(*Z*)-Caryophyllene	---	0.1	0.1	---	---	---	---	---	---	---
1420	(*E*)-Caryophyllene	5.8	7.8	9.0	6.7	4.1	4.1	4.2	7.4	11.3	8.8
1429	β-Copaene	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2
1436	α-*trans*-Bergamotene	0.4	0.5	0.3	---	1.7	1.3	1.4	0.7	---	0.2
1453	α-Humulene	12.6	22.7	28.0	17.2	16.9	17.4	17.4	41.6	51.2	32.5
1460	(*E*)-β-Farnesene	4.4	5.7	4.6	---	5.0	8.0	8.1	---	---	---
1471	(2*E*)-Dodecen-1-ol	---	---	---	---	0.2	---	---	---	---	---
1475	*trans*-Cadina-1(6),4-diene	---	---	---	---	---	---	---	---	0.1	0.1
1477	Geranyl propionate	1.7	---	---	---	---	---	---	---	---	---
1479	γ-Muurolene	---	1.7	1.1	0.5	1.2	0.7	0.7	0.4	1.1	0.6
1482	α-Amorphene	0.1	0.1	0.1	---	tr	0.1	---	0.1	0.1	0.1
1483	*ar*-Curcumene	---	---	---	---	0.2	0.1	0.1	---	---	---
1488	β-Selinene	1.2	1.1	0.4	0.6	0.6	0.3	0.4	0.2	0.3	0.3

Table 1. Contd.

1491	Neryl isobutyrate	---	---	---	---	---	---	---	---	---	trace
1493	δ-Selinene	---	1.2	0.7	0.8	0.6	0.4	0.4	0.5	0.7	0.7
1496	α-Selinene	1.8	---	---	---	---	---	---	---	---	---
1496	2-Tridecanone	---	0.7	0.9	---	1.6	0.8	0.9	---	0.5	---
1500	α-Muurolene	0.5	0.5	0.4	0.3	0.6	0.4	0.4	0.3	0.4	0.3
1507	(*E*,*E*)-α-Farnesene	0.4	0.4	0.4	0.1	0.9	0.5	0.5	0.1	0.4	0.2
1513	γ-Cadinene	---	1.1	1.5	0.9	1.9	1.0	1.0	0.7	1.2	0.9
1517	Geranyl isobutyrate	2.1	1.1	0.2	---	---	---	---	---	---	---
1524	δ-Cadinene	1.5	1.9	2.3	1.1	1.2	1.4	1.3	1.3	2.4	1.6
1524	*trans*-Calamenene	---	---	---	---	1.2	---	---	---	---	---
1532	*trans*-Cadina-1,4-diene	0.1	0.1	0.1	---	---	0.1	tr	0.1	0.1	0.1
1537	α-Cadinene	0.1	0.2	0.2	0.1	tr	0.1	0.1	0.1	0.2	0.1
1542	α-Calacorene	0.2	0.4	0.4	0.1	tr	0.3	0.3	0.1	0.2	0.1
1563	(*E*)-Nerolidol	---	0.3	0.1	---	---	---	---	0.1	---	0.1
1571	Dendrolasin	---	---	---	---	---	---	---	0.1	---	---
1583	Caryophyllene Oxide	0.9	2.2	2.2	0.9	3.0	1.3	1.3	0.6	0.7	1.2
1597	α-Humulene hydrate	0.4	0.7	1.0	0.3	2.9	1.4	1.3	0.3	0.5	0.4
1609	Humulene epoxide II	1.4	3.9	4.0	1.8	7.9	4.7	4.0	2.4	2.5	3.7
1626	1-*epi*-Cubenol	---	0.5	0.7	---	---	---	---	---	---	---
1630	Unidentified	0.4	1.7	2.1	0.6	9.7	3.9	3.7	0.7	0.9	0.7
1634	Caryophylla-4(12),8(13)-dien-5-ol		0.2	0.3	0.1	0.7	0.2	0.3	0.1	0.1	0.1
1639	τ-Cadinol	0.2	0.3	0.5	0.2	1.1	0.3	0.3	0.2	0.3	0.2
1643	α-Muurolol	---	---	---	tr	---	---	---	tr	tr	0.1
1652	α-Cadinol	0.2	0.3	0.3	0.2	1.2	0.3	0.3	0.1	0.2	0.1
1655	Unidentified	0.9	0.3	0.5	0.2	1.8	0.5	0.5	0.1	0.1	0.1
1660	Unidentified	0.5	0.8	0.5	0.4	3.5	1.1	1.1	0.3	0.8	0.2
1668	14-Hydroxy-(*E*)-caryophyllene	---	0.6	0.8	0.2	0.7	---	---	tr	0.5	0.2
1671	Cadalene	---	---	---	---	0.4	---	---	---	---	tr
1671	(6*Z*)-Pentadecen-2-one	0.2	---	---	---	2.5	0.6	0.6	---	---	---
1699	2-Pentadecanone	---	---	---	---	0.8	0.1	0.1	---	---	---
1722	(2*Z*,6*E*)-Farnesol	0.2	0.2	0.3	0.2	0.9	0.2	0.2	0.4	0.3	0.7
1952	Palmitic acid	---	---	---	---	tr	0.5	0.4	---	---	---
Total identified		97.8	93.9	93.6	96.2	83.6	97.3	94.8	99.0	96.8	98.1
Monoterpene hydrocarbons		52.0	25.7	21.6	54.5	9.4	28.2	28.1	36.8	17.2	40.9
Sesquiterpene hydrocarbons		29.6	46.5	50.8	29.1	37.0	36.6	36.8	54.1	70.3	47.3
Oxygenated monoterpenoids		1.7	2.6	3.5	1.3	0.8	1.9	1.9	1.4	0.4	1.1

Table 1. Contd.

Oxygenated sesquiterpenoids	3.3	9.2	10.1	3.9	18.4	8.5	7.7	4.5	5.1	6.9
Aliphatic ketones	0.5	1.5	2.3	0.4	8.8	8.9	5.9	0.7	1.2	0.1
Aliphatic alcohols	0.9	0.7	0.4	1.1	0.8	1.0	0.9	0.2	0.0	0.2
Carboxylic esters	9.1	7.6	4.8	5.7	5.6	5.8	5.9	1.2	1.5	1.6
Carboxylic acids	0.4	0.0	0.0	0.0	1.6	5.1	6.4	0.0	0.0	0.0
Aldehydes	0.3	0.2	0.1	0.3	1.1	1.3	1.1	0.0	1.1	0.0

[a]Percent composition determined from total ion current count without correction. [b]RI = "Retention Index", determined with respect to a series of normal alkanes.

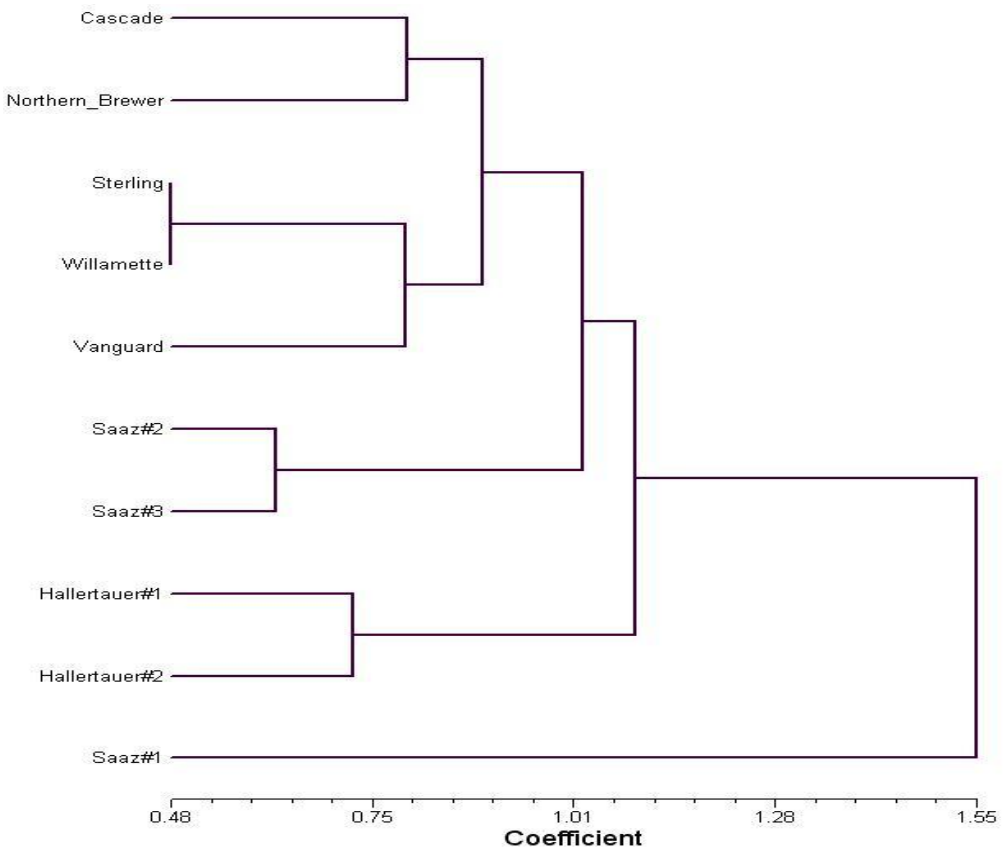

Figure 1. Dendrogram obtained by cluster analysis of the percentage composition of essential oils from finishing hops samples, based on correlation and using the Unweighted Pair-Group Method with Arithmetic Average (UPGMA).

study were either predominantly monoterpene-rich (Cascade, Northern Brewer) or sesquiterpene-rich (Hallertauer, Saaz, Sterling, Vanguard).

SUMMARY AND CONCLUSIONS

Aromas are very complex and subtle differences in component concentrations in complex mixtures can result in variable fragrance perceptions. Essential oils are particularly notable in this respect and hops are an excellent example. Nevertheless, some generalizations based upon this study can be made. Hop oil rich in sesquiterpene hydrocarbons tend toward earthy, herbal, woody, or spicy aromas while those dominated by monoterpenoids are more fruity or citrusy. Geranyl esters seem to provide additional floral and fruity characteristics to the odor. The cluster analysis (Figure 1) reveals a close chemical relationship between Sterling and Willamette and to some extent, Vanguard. Cascade and Northern Brewer also show similarities with each other. Interestingly, the U.S. varieties (Cascade, Northern Brewer, Sterling, Willamette, and Vanguard) form a cluster separated from the Old World varieties, Saaz and Hallertauer.

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