Direct Thermal Desorption−Gas Chromatography and Gas Chromatography−Mass Spectrometry Profiling of Hop (*Humulus lupulus* L.) Essential Oils in Support of Varietal Characterization

Sanja Eri,[†] Bin K. Khoo,[‡] Joseph Lech,[‡] and Thomas G. Hartman*[,†,‡]

Department of Food Science, Cook College, Rutgers, The State University of New Jersey, 65 Dudley Road, New Brunswick, New Jersey 08901-8520, and Center for Advanced Food Technology, Cook College, Rutgers, The State University of New Jersey, 63 Dudley Road, New Brunswick, New Jersey 08901-8520

The use of direct thermal desorption−gas chromatography−mass spectrometry (DTD-GC-MS) and DTD-GC−flame ionization detection (DTD-GC-FID) for characterization of hop essential oils is described. Four hop varieties (Nugget, Galena, Willamette, and Cluster) from the Yakima valley (Yakima, WA) 1998 harvest were analyzed by DTD-GC-MS and DTD-GC-FID methodology. Approximately 1 g of hops was needed for the analysis. Hop samples were prepared for GC-MS and/or GC-FID profiling in ∼20 min. More than 100 volatile compounds have been identified and quantified for each hop variety. The results were found to be in good agreement with conventional steam distillation−extraction (SDE) data. A calibration curve for determination of essential oil content in hops by DTD-GC-FID has been generated. Quantitation of hop oil content by DTD-GC-FID was shown to be in good agreement with conventional SDE data. The recovery of key oil components valuable for varietal identification was demonstrated to be highly reproducible and characteristic of each variety analyzed when DTD-GC-FID was used for analysis.

Keywords: *Hops; Humulus lupulus L.; essential oils; direct thermal desorption (DTD); GC-MS*

INTRODUCTION

Among the flavor characteristics that most distinguish beer from other alcoholic beverages are hop aroma and bitterness. Whereas bitterness is derived from reaction products of so-called alpha and beta hop acids, hop aroma is a complex mixture of a few hundred volatile compounds derived from the essential oil of hops (Grant, 1995). Because the composition of hop oil contributes to the aroma of beer, the essential oil profile of hop samples contains valuable information for brewers. It has been established that the composition of hop oil depends on the hop variety (Likens and Nickerson, 1967). Confirmation of a hop variety calls for the comparison of a hop oil profile with a varietal database. The variety of a hop sample of unknown origin is established on the basis of the presence and amount of key oil components (Buttery, 1967; Kenny, 1990; Peacock and McCarty, 1992; Perpete, 1998). In both cases, the analyst has to have a reliable, reproducible, and preferably rapid analytical method that will confirm a variety is the one claimed or, in the case of an unknown sample, is correctly identified.

Gas chromatography and mass spectrometry are successfully employed for identification and quantification of hop essential oil components. However, their efficiency is limited by the excessively long time needed to prepare a sample. The most common methods for isolating essential oils from hops are based on steam distillation (Nickerson and Likens, 1966; Katsiotis et al., 1989; Green and Osborne, 1992), extraction with organic solvents (Lam et al., 1986), and extraction with carbon dioxide (Langezaal et al., 1990). With these techniques it takes hours to prepare a sample. Steam distillation requires complex glassware, the assembly, disassembly, and cleaning of which consume additional time. Steam distillation also requires large amounts of sample. The recovery of oil components, moreover, is dependent on the length of the distillation process, and there can be distortion of hop oil composition as demonstrated by Pickett et al. (1975, 1977). Solvent extraction methods have the disadvantage that they typically extract nonvolatile resinous components along with the essential oil, which adversely affect GC columns. Carbon dioxide extraction methods require special and expensive equipment. The recovery of oil components is greatly influenced by the extraction conditions, and the extracts also contain high-boiling or nonvolatile residues that adversely affect GC columns.

Direct Thermal Desorption (DTD). DTD permits the analysis of solid samples without any prior solvent extraction or other time-consuming sample preparation. In this technique samples are placed directly into a glass-lined stainless steel desorption tube, which is subjected to controlled heating in a flow of inert carrier gas. The desorbed volatiles are transferred directly into the GC for analysis in a one-step process. Description and different applications of DTD have been published by Hartman et al. (1991, 1992), Manura and Hartman (1992), and Grimm et al. (1998).

The purpose of this study was to test the DTD methodology for essential oil profiling of hops. The method is simple, requires small amounts of sample,

* Address correspondence to this author at the Center for Advanced Food Technology, Cook College, Rutgers, The State University of New Jersey, 63 Dudley Road, New Brunswick, NJ 08901-8520 [telephone (732) 932-8306, ext. 310; fax (732) 932-8690; e-mail thartman@aesop.rutgers.edu].

[†] Department of Food Science.

[‡] Center for Advanced Food Technology.

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and was expected to provide good recovery of oil components while offering a significant time reduction when compared to other methods currently in use. To validate DTD as an alternative method for hop essential oil analysis, the hop samples were also analyzed by conventional simultaneous steam distillation−extraction (SDE).

EXPERIMENTAL PROCEDURES

Material. Dried cones of four hop varieties (Nugget, Galena, Willamette, and Cluster) were gifts from Yakima Chief Ranches, Inc., WA. Hops were from the 1998 Washington State Yakima valley crop. Each hop variety was from a single growth. The hop samples were sealed in freezer bags and stored frozen for a short period until analysis.

Absorbent Tenax TA, 60/80 mesh, as well as Chromosorb W-HP, 80/100 mesh (used as chromatographic support), and silanized glass wool, were obtained from Supelco, Inc. (Bellefonte, PA).

Internal standards toluene-d_8 and naphthalene-d_8 were obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI).

Solvents methanol and dichloromethane were from Fischer Scientific, Inc. (Springfield, NJ).

Glass-lined thermal desorption tubes used for DTD were obtained from Scientific Instrument Services, Inc. (Ringoes, NJ).

Sample Preparation. Silanized glass-lined stainless steel desorption tubes (4.0 mm i.d. × 10 cm) were packed with a 2 cm bed volume of Tenax TA adsorbent between plugs of silanized glass wool. To ensure that they were free of any contaminants, the tubes were preconditioned by passing nitrogen through them at a rate of 40 mL/min while they were held at 320 °C for 1 h. The small bed of Tenax is required to trap internal standard, which is injected prior to analysis, and to prevent loss of hop volatiles during the preheating purge step of the analysis.

Individual hop samples were ground into fine powder by crushing ∼1 g of dried cones using a mortar and pestle. Aliquots (0.5 g) of powdered hops were mixed with 4.5 g of 80/100 mesh Chromosorb (preconditioned at 180 °C for 8 h to remove any volatiles present) and homogenized for 30 s in a cryogenically cooled micro-mill (Bell-Art Products, Pequannock, NJ). Chromosorb W-HP is used to prevent loss of volatiles, as a diluant to ground samples due to the small volume of the sample needed for the analysis, and to promote optimal flow conditions through the desorption tube. Portions of the homogenates produced in this process (∼100 mg) were measured into desorption tubes above the Tenax adsorbent bed and plugged with silanized glass wool. The loaded sample desorption tubes were spiked with 9.8 μg of toluene-d_8 and 9.9 μg of naphthalene-d_8 as internal standards, using a solvent flush technique. The samples were then analyzed by short-path DTD-GC-FID and DTD-GC-MS for volatile oil profiling (Hartman et al., 1991, 1992; Manura and Hartman, 1992; Grimm et al., 1998).

DTD-GC. DTD was performed using the model TD-2 short-path thermal desorption unit (Scientific Instrument Services, Inc., Ringoes, NJ), which was placed directly on the injection port of the gas chromatograph. The loaded sample desorption tube was attached to the TD apparatus and purged with helium for 1 min to remove all traces of oxygen. The sample was then injected into the GC. Preheating injection time (during which GC carrier gas is replaced by carrier gas from the TD apparatus) was 1 min. Preheated (150 °C) heater blocks were then closed around the desorption tube, and the sample was thermally desorbed at 150 °C for 5 min. Due to the heat applied and the inert gas flow through the desorption tube, volatiles from the sample were transferred into the GC injection port and column.

The gas chromatograph used in the study was a Varian 3400 with a flame ionization detector. The column used was a capillary column (DB-1, 60 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA). The carrier gas was helium with a flow rate of 1.0 mL/min, and a split ratio of 100:1 was employed. The injection port temperature was 220 °C, and the detector temperature was 320 °C. The column temperature was programmed from −20 °C (held for 5 min during the thermal desorption interval to achieve cryofocusing) to 100 °C at a rate of 10 °C/min, then to 200 °C at a rate of 4 °C/min, and finally to 280 °C at a rate of 10 °C/min.

The chromatograms were recorded and processed using a Peak Simple Chromatographic Data System (SRI Instruments, Torrance, CA).

Retention indices of essential oil components were calculated using the equation for multistep temperature programs as described by Majlat (1974) with the data obtained by injecting a C5−C26 *n*-paraffin standard using the same analytical conditions as the samples.

DTD-GC-MS. For the DTD-GC-MS analysis, the conditions were the same as described for DTD-GC analysis except that the end of the GC capillary column was inserted directly into the ion source of the mass spectrometer via a heated transfer line maintained at 280 °C. The mass spectrometer was a Finnigan MAT 8230 high-resolution, double-focusing, magnetic sector instrument. The mass spectrometer was operated in the electron ionization (EI) mode, scanning masses 35−350 amu once each 0.6 s with a 0.8 s interscan time. Analyses were also performed in chemical ionization (CI) mode using isobutane as a reagent gas with an ion source temperature of 250 °C. In this instance a mass range of 60−600 amu was scanned.

The mass spectrometric data were acquired and processed using a Finnigan MAT SS 300 data system. Mass spectra obtained by electron ionization were background-subtracted and library-searched against the National Institute of Standards and Technology (NIST) mass spectral reference collection. The identification of oil components was confirmed by interpretation of electron ionization and chemical ionization MS data, by comparison to the NIST database and published literature (Buttery and Ling, 1967; Katsiotis et al., 1989; Maarse and Visscher, 1989; Kenny, 1990; Peacock and McCarty, 1992; Perpete, 1998), and by GC retention index (Jennings and Shibamoto, 1980).

Hop Oil from Steam Distillation. Hop oil was isolated according to the method of Nickerson and Likens (1966) with dichloromethane as a solvent to ensure better recovery of oxygenated compounds. Hop samples (100 g) were mixed with 2000 mL of distilled water and distilled−extracted for 4 h in a simultaneous SDE apparatus (Likens and Nickerson extractor, Kontes, Vineland, NJ) with dichloromethane (150 mL) as solvent. Distillates were concentrated to ∼5 mL in a Kuderna-Danish concentrator with a three-ball Snyder column. The remaining solvent was removed by a gentle stream of nitrogen at room temperature. The oil content was measured gravimetrically, and the sample extracts were stored under nitrogen at −40 °C until analyzed. Injection volumes of 0.2 μL were analyzed by GC and GC-MS with a split ratio of 200:1. GC and MS conditions were the same as described for DTD analysis.

Hop Oil Content Determination by DTD-GC-FID. Essential oil content of selected hops by DTD-GC-FID was determined from a calibration curve generated by spiking desorption tubes (packed with a 2 cm bed volume of Tenax TA adsorbent) with six concentrations of Galena hop oil (one point below and one point above literature-reported essential oil content of hops) in methanol containing a constant amount of internal standard (9.8 μg of toluene-d_8 and 9.9 μg of naphthalene-d_8). The calibration curve was generated using linear regression analysis of total peak area divided by internal standard (naphthalene-d_8) peak area versus hop oil content in percent w/w.

RESULTS AND DISCUSSION

Essential oil components of four hop varieties used in the study were identified by DTD-GC-MS and by SDE-GC-MS and quantified by DTD-GC-FID and SDE-GC-FID. Example gas chromatograms obtained by both

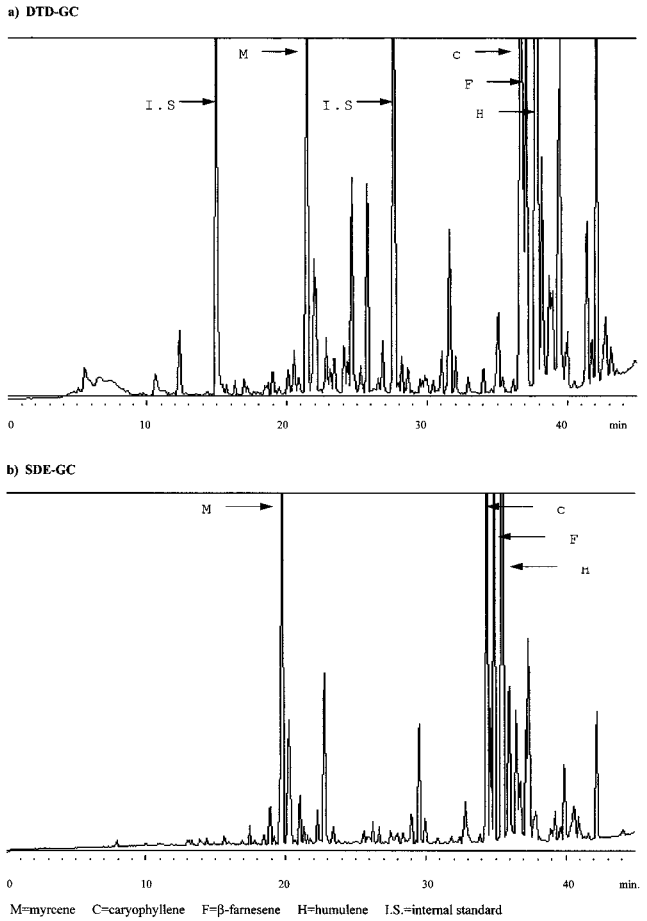

Figure 1. Chromatograms of Willamette hops obtained by DTD-GC and SDE-GC.

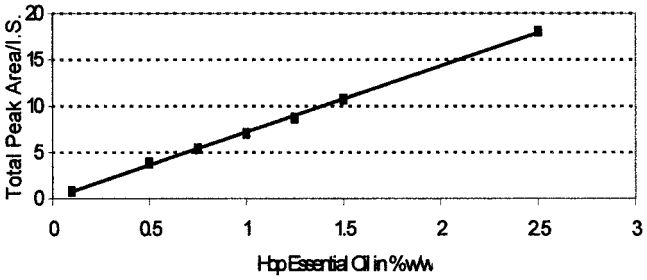

Figure 2. Hop essential oil calibration curve by DTD-GC-FID analysis.

of these methods for the Willamette variety are shown in Figure 1. Major compound peaks are labeled on both chromatograms, and their relative amounts as determined by the DTD-GC-FID method are seen to be in excellent agreement with the SDE-GC-FID data. It should be noted that there is no internal standard in SDE samples. Internal standard was added to DTD samples for the purpose of hop oil content determination.

Four replicate analyses were performed by DTD-GC-FID. Relative percentages of the volatiles based on the area integration were calculated for each replicate, and the averages were determined.

The identification and relative percentages of volatile compounds from each of the four hop varieties are listed in Table 1.

A calibration curve that was generated for determination of essential oil content in hops by DTD-GC-FID analysis is shown in Figure 2. The linear regression equation had a coefficient of determination (R^2) of 0.99. Hop oil content in each of the four hop varieties as determined by DTD-GC-FID and by SDE method (gravimetrically) is shown in Table 2. Hop oil content was higher when determined by DTD-GC-FID. The trends were in agreement with SDE results in which the Nugget cultivar has the highest amount of essential oil and is followed by Galena hops, Willamette hops, and Cluster hops in order of decreasing essential oil content.

Several keys for varietal characterization of hops have been published (Buttery and Ling, 1967; Kenny, 1990; Peacock and McCarty, 1992). They are based on the differences in the presence and amounts of some essential oil compounds found in different hop varieties. In addition, ratios of selected hop oil compounds have been proven to be useful for distinguishing among hop varieties. The ratios of some key oil compounds as determined by DTD-GC-FID and SDE-GC-FID methods are shown in Table 3. Four replicate analyses were performed for each hop variety by DTD-GC-FID. Ratios of peak areas were calculated for each analysis, and averages and standard deviations were calculated for each variety.

Generally good agreement between DTD and SDE data was observed for a majority of the volatiles present in the hops studied. However, there are three compounds for which the recovery by DTD was significantly more than that of SDE. These are caryophyllene oxide; peak 251 (as referred to Table 1) with a retention index of 1865 (unknown 220 MW unsaturated alcohol or acid), and peak 253 with a retention index of 1868 (unknown 220 MW oxygenated sesquiterpene).

Higher recovery of oxygenated compounds in the DTD data could mean that DTD is harsher and causing oxidation of hop compounds. DTD is performed at a temperature of 150 °C to ensure quantitative delivery of volatiles adsorbed on Tenax TA. This is 50 °C higher than the temperature at which SDE is performed. However, DTD is performed in an inert atmosphere, with no oxygen present. Higher recovery of oxidation products could, therefore, mean that DTD offers better recovery of oxygenated compounds, which tend to be more polar and high boiling. Better extraction efficiency may also contribute to the result.

To the best of our knowledge, 14 of the volatiles reported in Table 1 are reported in hops for the first time. These compounds are formic acid; acetic acid; isopentyl acetate; 1,3-nonadiene; glycerol; α-terpinene; phenol; isooctanol; pentyl 3-methylbutyrate; 3-hexenyl isobutyrate; 1,3,5-undecatriene; isocaryophyllene; 1,2,3,4,-4A,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)naphthalene (CAS Registry No. 16728-99-7); 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one; and hexadecanoic acid (palmitic acid). Among them, isopentyl acetate, α-terpinene, isooctanol, pentyl 3-methylbutyrate, 1,3-nonadiene, 3-hexenyl isobutyrate, isocaryophyllene, and 1,2,3,4,4A,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene are found in both DTD and SDE data. Formic acid, acetic acid, glycerol, phenol, 1,3,5-undecatriene, and 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one have been found only in samples analyzed by DTD, whereas hexadecanoic acid has been found only in SDE data. Among the compounds present only in DTD data, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one is known to be an artifact formed during thermal desorption by dehydration and thermal degradation of sugar. Glycerol is known to be too water

Table 1. Identities and Relative Percentages of Volatile Compounds in Selected Hops As Determined by DTD and SDE

			relative percentages of volatiles in selected hop varieties							
			Nugget		Galena		Willamette		Cluster	
peak	compound[a]	RI	DTD[b,c]	SDE[d]	DTD	SDE	DTD	SDE	DTD	SDE
1	acetone								tr[e]	tr
2	isoprene				0.108	0.461	0.134	0.037	0.213	0.020
3	2-methyl-3-buten-1-ol		0.087	0.016	0.065	0.149	0.027	0.018	0.149	0.068
4	formic acid*		0.006						0.008	
5	3-methylbutanal	614			0.014	0.158			0.004	0.033
6	acetic acid*	674	0.347		0.193		0.488		0.427	
7	isopentyl alcohol	681			0.036	0.045	0.018	0.024	0.022	0.048
8	2-hexanone	684			0.014	0.030	0.010	0.023	0.011	0.047
9	3-methyl-2-pentanone	697			**	0.043	**	0.022	0.030	0.027
10	3-methyl-2-butenal	753	0.061	0.011	0.074	0.091	0.055	0.032	0.118	0.075
11	3-methyl-2-buten-1-ol	762	0.027	0.011	0.016	0.045	tr	0.005	0.044	0.017
12	hexanal	776	0.003	0.011	0.005	0.026	0.042	0.036	0.005	0.056
13	furfural	782	tr	0.001						
14	octane	798	0.065	0.008	0.043	0.039	0.050	0.018	0.076	0.029
15	3-methylbutanoic acid	825	0.141		0.112		0.078		0.009	
16	3-methylbutanoic acid + butyric acid	826		0.042		0.015		trs		0.014
17	butyric acid	830	0.010		0.028		tr		0.015	
18	2-hexenal	839		0.027		0.026		0.058		0.087
19	2-methylbutanoic acid	842			0.004	0.011			0.019	0.065
20	2-hexenal + isobutyl propanoate	843	0.038		0.070		0.039		0.080	
21	isobutyl propanoate	848		0.013		0.053		0.012		0.065
22	isopentyl acetate*	859	0.022	0.016	0.050	0.034			0.066	0.037
23	2-heptanone	870	0.009	0.006						
24	heptanal	878	0.034	0.021	0.028	0.023	0.032	0.025	0.078	0.053
25	unknown, 43 bp[f]	883					0.051	0.005		
26	possibly 108 MW dimethyl pyrazine isomer	888	0.019							
27	isobutyl isobutyrate	899	0.108	0.044	0.217	0.159	0.086	0.088	0.387	0.340
28	methyl hexanoate	905	0.041	0.018	0.010		0.008		0.022	0.035
29	methyl hexanoate + 2,6-dimethyl-2,5-heptadiene	905				0.050		0.012		
30	2,6-dimethyl-2,5-heptadiene	907	0.025	0.022	0.026		0.020		0.002	0.026
31	unknown, 69 bp	914	0.001	tr	0.037	0.015	0.031	0.030	0.067	0.051
32	1,3-nonadiene*	918	0.031	0.025	0.022	0.021			0.014	0.034
33	unknown thiol	919	0.009							
34	α-thujene	920	0.007	tr					0.007	0.001
35	α-pinene	937	0.105	0.035	0.120	0.064	0.142	0.054	0.202	0.114
36	pentanoic acid	938	tr	tr						
37	glycerol*	940	tr							
38	dimethyl trisulfide	947			tr	tr	tr	0.003	0.016	0.012
39	3-methylbutyl propanoate	949	0.166	0.071	0.071	0.045			0.086	0.038
40	2-methylbutyl propanoate	952	0.462	0.281	0.760	0.699	0.119	0.220	0.677	0.659
41	unknown	962	0.018	0.001			0.026	0.007		
42	6-methyl-5-hepten-2-one	963					0.087	0.060	tr	tr
43	methyl 5-methylhexanoate	963	0.044	0.030	0.341	0.336			0.072	0.049
44	unknown	965					tr	tr		
45	unknown unsaturated alcohol + methyl heptanoate (branched)	966					0.005	trs		
46	β-pinene	980			0.472	0.430	0.366	0.388	0.321	0.251
47	methyl heptanoate (branched)	983							0.683	0.716
48	β-pinene + methyl heptanoate (branched)	983	0.312	0.360						
49	β-myrcene	984	28.315	31.783	32.129	32.580	27.620	30.079	40.253	49.448
50	isobutyl isopentanoate	989	0.016	0.060	0.006	0.044			0.033	0.082
51	3-methylbutyl isobutyrate	996	0.648	0.406	0.558	0.534	0.069	0.078	0.535	0.416
52	2-methylbutyl isobutyrate	1001	1.027	0.674	2.220	1.828	0.412	0.584	2.322	2.274
53	methyl heptanoate	1004			0.349	0.262	0.420	0.449		
54	methyl heptanoate + methyl 4-heptenoate	1005	0.854	0.425					0.589	0.421
55	unknown sulfur-containing compound	1012					0.002			
56	α-terpinene*	1013	0.008	0.015	0.055	0.045	0.017	0.024	0.052	0.061
57	*p*-cymene	1018	0.006	0.006	0.007	tr				
58	phenol*	1026							0.054	
59	limonene + β-phellandrene	1028	0.280	0.344	0.289	0.401	0.255	0.321	0.419	0.567
60	unknown, 41 bp	1033							0.034	0.025
61	pentyl 2-methylpropanoate	1033	0.016	0.015	0.015	0.026	0.013	0.008		
62	2-nonanone (branched)	1034			tr	tr				
63	β-ocimene	1037	0.464	0.436	1.003	1.274	0.078	0.087	0.198	0.190
64	possibly methyl 2,5-dimethylhexanoate	1047	0.118				0.195	0.042		
65	possibly methyl 2,5-dimethylhexanoate + heptanoic acid	1048		0.047						
66	heptanoic acid	1048	0.008		0.061	0.021	0.011			0.062
67	heptanoic acid + γ-terpinene	1049							0.084	
68	heptanoic acid + γ-terpinene + isooctanol*	1049						0.053		
69	γ-terpinene	1051	0.011	0.007	0.009	0.019	0.002			0.013
70	isooctanol*	1051	0.005	0.008			0.007			
71	methyl 6-methylheptanoate	1068				0.824	0.158	0.184		0.505

Table 1. (Continued)

			relative percentages of volatiles in selected hop varieties							
			Nugget		Galena		Willamette		Cluster	
peak	compound[a]	RI	DTD[b,c]	SDE[d]	DTD	SDE	DTD	SDE	DTD	SDE
72	methyl 6-methylheptanoate + 2-nonanone	1069	0.213	0.168	0.828				0.651	
73	2-nonanone	1069				0.034	0.010	0.033		0.073
74	S-methyl hexanethioate	1075	0.069	0.015	0.021	0.001	0.011	tr	0.016	0.013
75	linalool oxide	1076	0.017	0.008	0.091	0.013	0.091	0.015	0.146	0.031
76	terpinolene	1085					0.010	0.011	0.005	0.012
77	2-nonanol + nonanal + linalool	1085	1.365	1.292						
78	nonanal + linalool	1086			0.332	0.342	0.917	1.068	0.624	0.658
79	unknown 150 MW compound, 69 bp	1087						tr		0.024
80	2-methylbutyl 2-methylbutyrate	1090	0.123	0.052	0.230	0.111	0.047	0.052	0.199	0.088
81	pentyl 3-methylbutyrate*	1093	0.153	0.069	0.208	0.032	0.022	0.019	0.238	0.065
82	methyl octanoate (branched)	1097	0.001	tr	tr	0.003				
83	methyl octanoate	1105	0.410	0.350	0.968	0.758	0.105	0.091	1.258	0.813
84	ethyl heptanoate	1108					0.019	0.027		
85	unknown 154 MW unsaturated compound	1110					tr	0.015		
86	unknown 130 MW ester, 57 bp	1110	0.020	0.006	0.074	0.003	tr	0.001	0.054	0.015
87	2,3-dihydro-3,5-dihydroxy-6-methyl-4*H* pyran-4-one*	1119	0.347		0.107		0.997		0.798	
88	octanoic acid (branched)	1122							0.023	0.012
89	unknown 136 MW terpene, 91 bp	1125			tr	0.005				
90	hexyl isobutyrate	1131	0.035	0.030			0.026	0.034	0.023	0.026
91	unknown 136 MW terpene, 121 bp + hexyl isobutyrate + 3-hexenyl isobutyrate*	1132			0.090	0.105				
92	3-hexenyl isobutyrate*	1138	0.025	0.014			0.010	0.012		
93	2-decanone (branched)	1139			0.041	0.043			0.042	0.046
94	unknown, 150 MW	1141								tr
95	octanoic acid	1142	0.015	0.022	0.132	0.055	0.064	0.010	0.222	0.113
96	methyl phenylacetate	1143	0.069	0.025				0.010		
97	methyl phenylacetate + unknown 130 MW branched alcohol, 59 bp	1150					0.249			
98	unknown 130 MW branched alcohol, 59 bp	1152	0.265		0.347				0.486	
99	unknown	1158						0.017		
100	1,3,5-undecatriene*	1170			0.009					
101	unknown 136 MW, 43 bp	1171						0.004		
102	unknown 136 MW, 69 bp	1172						tr		
103	unknown unsaturated compound	1173		0.016						
104	methyl nonanoate (branched)	1174	0.016	0.021	**	0.183			0.250	0.180
105	2-decanone	1175	**	0.025	**	0.038	**	0.082	**	0.044
106	α-terpineol + methyl 4-octenoate	1179						0.006		
107	methyl 4-octenoate	1181	0.012	0.043	0.212	0.143			0.026	
108	α-terpineol	1182	tr	tr					tr	
109	unknown, 136 MW	1183						tr		
110	methyl 4-octenoate + α-terpineol + unknown, 136 MW	1183					0.014			
111	methyl 4-octenoate + α-terpineol + decanal	1183								0.057
112	heptyl propanoate	1184			0.024	0.024	0.039	0.056		
113	2-decanol	1185	0.268	0.189						
114	decanal	1185							0.027	
115	methyl nonenoate isomer	1192	0.144	0.077	0.052	0.047	0.143	0.131	0.112	0.093
116	unknown, 100 bp	1193					0.025	0.017	0.021	0.034
117	methyl nonanoate	1205	0.460	0.332	0.443	0.349	0.098	0.100	0.334	0.243
118	unknown	1208								0.036
119	nerol	1213	0.024	0.021	0.015	0.011	0.019	0.016	0.042	0.037
120	2-methylheptyl propanoate	1230	0.060	0.040	0.039	0.049	0.045	0.074		
121	geraniol	1235	0.039	0.060	0.037	0.029	0.043	0.025	0.462	0.413
122	2-undecanone (branched)	1241	0.113	0.042	0.195	0.149	0.075	0.026	0.146	0.070
123	possibly methyl ester of methyl nonenoic acid	1243	0.020	0.015	0.009	tr	0.037	0.098		
124	decanoic acid (branched)	1245					tr	0.002	0.014	0.002
125	2-undecanol (branched)	1251	0.064	0.049						
126	unknown 43 bp unsaturated alcohol or acid	1257	0.068	0.084	0.140	0.150	0.065	0.075	0.137	0.147
127	unknown 43 bp unsaturated alcohol or acid	1264							0.016	0.018
128	methyl decanoate (branched)	1265					0.011	0.014		
129	unknown unsaturated alcohol (possibly undecenol isomer)	1266	0.309	0.215			0.009	0.012		
130	methyl decanoate (branched)	1270	0.090	0.072	0.619	0.595	0.025	0.038	0.373	0.316
131	2-undecanone	1274	0.379	0.430	0.641	0.642	0.170	0.185	0.734	0.719
132	2-undecanol	1287	0.841	0.492						
133	octyl propanoate	1284			0.062	0.040	0.030	0.018		
134	methyl 4-decenoate + methyl 4,8-decadienoate	1290	2.857	2.774	3.940	4.202	0.941	1.294	trs	0.006
135	unknown lactone	1296	tr	tr	tr	tr	0.006	0.006	4.022	4.655
136	methyl decenoate isomer	1298	0.008	0.007	0.025	0.026			0.018	0.026
137	methyl geranate	1302	0.035	0.083	0.036	0.063	0.152	0.137		0.033
138	methyl geranate + methyl decanoate	1306							1.381	
139	methyl decanoate	1306	0.246	0.166	1.752	1.497	0.015	0.015		1.025
140	octyl 2-methyl propanoate	1329	0.115	0.069	0.255	0.168	0.081	0.043	0.172	0.090

Table 1. (Continued)

			relative percentages of volatiles in selected hop varieties							
			Nugget		Galena		Willamette		Cluster	
peak	compound[a]	RI	DTD[b,c]	SDE[d]	DTD	SDE	DTD	SDE	DTD	SDE
141	possibly methyl 9-methyldecanoate	1340	0.023	0.014			0.007	0.011		
142	unknown unsaturated compound	1344							0.005	0.008
143	2-dodecanone (branched)	1345	0.007	0.001	0.152	0.118			0.174	0.120
144	2-dodecanone (branched)	1348			0.020	0.023				
145	methyl 2-undecenoate	1353			0.016	tr				
146	decanoic acid (branched)	1357					0.010	tr	0.014	0.021
147	α-cubebene	1360	0.082	0.040		0.023	0.101	0.054	0.050	0.023
148	α-cubebene + unknown unsaturated alcohol or acid, 43 bp	1360			0.102					
149	unknown terpene ester	1363				0.082				
150	unknown unsaturated alcohol or acid, 43 bp	1366				0.011				
151	unknown unsaturated alcohol or acid, 43 bp + 2-dodecanol (branched)	1368	0.076	0.055						
152	unknown, 194 MW, 95 bp	1368			tr		0.003	0.010	0.005	0.009
153	methyl undecanoate (branched)	1370							0.266	0.325
154	unknown, 43 bp	1375					0.010	0.044		
155	unknown, 194 MW, 95 bp + methyl undecanoate (branched)	1375				0.622				
156	methyl undecanoate (branched)	1375			0.450					0.087
157	methyl undecanoate (branched) + 2-dodecanone	1377							0.074	
158	2-dodecanone	1377	0.089	0.151	0.065	0.203	0.019			
159	2-dodecanone + α-ylangene	1382						0.092		0.145
160	α-ylangene + decanoic acid (branched)	1383				0.116				
161	decanoic acid (branched)	1386			0.067					
162	α-ylangene	1386	0.084	0.104	0.065		0.080		0.058	
163	copaene	1391	0.255		0.262	0.356	0.307	0.258		0.182
164	copaene + methyl undecenoate isomer	1395							0.208	
165	methyl undecenoate isomer	1396						0.015		0.020
166	unknown 204 MW sesquiterpene, 81 bp	1397						0.037	0.066	0.051
167	methyl undecenoate + 204 MW sesquiterpene, 81 bp + methyl undecadienoate	1397					0.027			
168	methyl undecadienoate isomer + unknown 204 MW sesquiterpene, 91 bp	1398			0.150	0.139		0.023		
169	methyl undecenoate isomer	1399						0.014		
170	methyl undecenoate isomer + unknown 204 MW sesquiterpene, 91 bp	1399					0.059			
171	copaene + germacrene D + unknown 204 MW sesquiterpene, 105 bp	1400		0.354						
172	germacrene D	1401	0.057							
173	unknown	1402							tr	tr
174	methyl undecenoate isomer	1403			0.057	0.072				
175	unknown 204 MW sesquiterpene, 105 bp	1404	0.023		0.013	0.016			tr	
176	methyl undecanoate	1410	0.010	0.033	0.045	0.056			0.027	0.048
177	isocaryophyllene*	1413	0.030	0.030	0.005	0.004	0.057	0.068	0.043	0.068
178	unknown terpene ester	1415		0.059						
179	calarene	1416	0.005	0.003						
180	unknown 204 MW sesquiterpene, 91 bp	1417					tr	tr	tr	0.008
181	unknown 204 MW sesquiterpene, 93 bp	1422					0.006	0.009		
182	caryophyllene	1423	14.586	15.323	12.265	10.954	13.793	11.708	9.225	6.915
183	*β*-cubebene	1426	0.583	0.390	0.515	0.370			0.452	0.274
184	*β*-cubebene + α-bergamotene	1427					1.194	0.955		
185	2-tridecanone (branched)	1432	0.010		0.019	0.010	tr	tr	0.027	0.042
186	2-tridecanone (branched) + unknown unsaturated compound, 43 bp	1433		0.034						
187	unknown unsaturated compound, 43 bp	1435								0.358
188	2-tridecanone (branched) + *β*-farnesene	1436					3.138			
189	*β*-farnesene	1439	0.014	0.061	0.018	0.156		8.592	tr	tr
190	unknown 204 MW sesquiterpene, 105 bp	1456	0.021	0.030	0.030		0.025	0.038	0.027	
191	unknown 204 MW sesquiterpene, 105 bp	1458	0.020	0.011	0.047		0.034	0.038	0.024	
192	2 unknown 204 MW sesquiterpenes, 105 bp + humulene	1460				20.272				15.204
193	unknown terpene ester	1462		tr				0.049		
194	humulene	1463	29.563	28.564	22.663		35.143	32.474		
195	humulene + methyl dodecenoate isomer	1466							19.337	
196	acetate of unsaturated alcohol (possibly decadienol isomer)	1467								tr
197	unknown 204 MW sesquiterpene, 161 bp	1468	0.231						0.118	tr
198	methyl dodecanoate (branched)	1469				0.350			tr	tr
199	methyl dodecanoate (branched) + unknown 204 MW sesquiterpene, 161 bp	1469			0.164		0.096	0.037		
200	methyl dodecenoate isomer	1469	tr		tr					1.314
201	unknown 204 MW sesquiterpene, 161 bp + methyl dodecenoate isomer + 2-tridecanone	1476		0.449						

Table 1. (Continued)

			relative percentages of volatiles in selected hop varieties							
			Nugget		Galena		Willamette		Cluster	
peak	compound[a]	RI	DTD[b,c]	SDE[d]	DTD	SDE	DTD	SDE	DTD	SDE
202	unknown 204 MW sesquiterpene, 161 bp + 2-tridecanone	1476				1.274				
203	2-tridecanone	1477						0.115		
204	2-tridecanone + γ-cadinene	1477					1.098			
205	2-tridecanone + γ-cadinene + unknown 204 MW sesquiterpene, 189 bp + α-amorphene	1478	1.221		1.769				0.899	0.584
206	methyl dodecenoate isomer + unknown 204 MW sesquiterpene, 189 bp + α-amorphene	1478				1.001				
207	γ-cadinene	1479				3.683		1.181		
208	γ-cadinene + unknown 204 MW sesquiterpene, 189 bp + α-amorphene	1480		1.469						
209	α-amorphene	1481					0.108			
210	methyl 3,6-dodecadienoate	1482	tr	tr	0.334					
211	α-amorphene + α-farnesene	1485						0.904		
212	α-farnesene	1487	0.001	0.075			0.055			
213	methyl 3,6-dodecadienoate + β-selinene	1492				1.872				
214	unknown terpene ester	1496		0.455		0.129		0.169		0.586
215	β-selinene	1502	1.675	1.987	1.593		0.592	0.118	0.851	0.614
216	unknown 204 MW sesquiterpene, 119 bp	1504					tr	tr		
217	γ-muurolene	1508	0.326	0.262	0.357		0.438		0.279	0.098
218	γ-muurolene + γ-selinene	1511				1.563		0.420		
219	γ-selinene	1512	1.511	1.751	1.458		0.364		0.694	0.609
220	methyl dodecanoate	1514			tr	tr			tr	
221	methyl dodecanoate + δ-cadinene	1516								0.057
222	δ-cadinene	1516	0.063	0.102	0.072	0.088	0.048		0.033	
223	δ-cadinene + unknown, 69 bp	1521						0.052		
224	α-muurolene	1527	0.782	0.823	0.815	0.695	0.992	0.831	0.552	0.373
225	calamenene	1530	tr	tr	tr	tr	tr	tr	tr	tr
226	cadinene	1533	1.134	1.516	1.201	1.359	1.530	1.423	0.831	0.746
227	selina-3,7-diene	1538	0.121	0.235	0.120	0.205	0.110	0.170	0.090	0.130
228	1,2,3,4,4A,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene (CAS Registry No. 16728-99-7)*[g]	1546	0.092	0.172	0.092	0.148	0.134	0.154	0.067	0.090
229	unknown, 200 MW, 157 bp	1550	tr	tr	tr	tr	tr	tr	tr	tr
230	unknown 204 MW cadinene type sesquiterpene, 105 bp	1552	0.167	0.248	0.180	0.240	0.214	0.208	0.121	0.094
231	unknown, 43 bp, unsaturated compound	1554				0.053		0.014		0.085
232	possibly humulene epoxide isomer	1557			0.025	0.032				
233	unknown farnesene type sesquiterpene, 93 bp	1557					0.058	0.033		
234	unknown 222 MW, 43 bp, unsaturated compound (possibly acetate)	1559				0.176		0.018		0.131
235	unknown 234 MW oxygenated sesquiterpene, 91 bp	1562		0.009						
236	234 oxygenated sesquiterpene, 91 bp + 210 MW unsaturated alcohol or acid, 43 bp	1563	0.019							
237	unknown 210 MW unsaturated alcohol or acid, 43 bp	1563		0.085						
238	long-chain 2,4-dione compound (possibly 2,4-tridecadione)	1570		0.015						
239	unknown 224 MW unsaturated alcohol or acid, 43 bp	1570				0.013				
240	caryophyllyl alcohol	1572	0.062		0.019	0.024	0.010	0.096	0.040	0.016
241	possibly humulene epoxide isomer	1579							tr	tr
242	2-tetradecanone	1594	0.007	0.177					0.046	0.044
243	caryophyllyl alcohol + unknown 220 MW oxygenated sesquiterpene, 91 bp	1595		0.111						
244	unknown 220 MW oxygenated sesquiterpene, 91 bp	1600	0.100		0.100	0.179	0.111	0.025	tr	tr
245	caryophyllene oxide	1813	0.847	0.127			0.768	0.195	0.593	0.115
246	caryophyllene oxide + methyl tridecenoate isomer	1813			0.675					
247	methyl tridecenoate isomer	1821							tr	0.015
248	caryophyllene oxide + methyl tridecenoate isomer + humulene epoxide isomer	1824				0.039				
249	humulene epoxide isomer	1836	0.002	tr	0.084		0.184	0.089	0.068	0.090
250	unknown 224 MW unsaturated alcohol or acid, 43 bp	1863	0.178	0.118	0.056	0.052	0.055	0.097	0.074	0.196
251	unknown 220 MW unsaturated alcohol or acid, 43 bp	1865	0.932	0.042			1.800	0.499	0.917	0.173
252	220 MW unsaturated alcohol or acid, 43 bp + unknown sesquiterpenes, 43 and 105 bp	1868			1.159	0.106				
253	unknown 220 MW oxygenated sesquiterpene, 105 bp	1868	0.621	0.025					0.306	0.046
254	unknown	1886			tr	tr	tr	0.038	tr	0.044
255	unknown oxygenated sesquiterpene, 119 bp	1888			0.009	0.011				
256	humulene epoxide or diepoxide	1891	0.010	tr						
257	cadinol isomer, 119 bp		0.047	0.019	0.051	0.059	0.056	0.075	0.042	0.049
258	unknown 222 MW oxygenated sesquiterpene, 105 bp		0.074	0.051	0.197	0.023	0.151	0.092	0.039	0.033
259	δ-cadinol		0.329		0.175		0.307	0.103	0.250	
260	δ-cadinol + unknown 222 MW unsaturated alcohol or acid, 43 bp			1.120						
261	unknown 222 MW oxygenated sesquiterpene, 43 bp								0.006	tr
262	unknown oxygenated sesquiterpene, 105 bp								tr	tr

Table 1. (Continued)

peak	compound[a]	RI	relative percentages of volatiles in selected hop varieties							
			Nugget		Galena		Willamette		Cluster	
			DTD[b,c]	SDE[d]	DTD	SDE	DTD	SDE	DTD	SDE
263	δ-cadinol + α-cadinol					0.055				0.073
264	humulene epoxide isomer		0.004	tr	0.006					
265	α-cadinol		0.130	0.089	0.148		0.158	0.212	0.046	
266	juniper camphor		0.185	0.032	0.176	0.018			0.047	tr
267	humulene epoxide isomer		0.004	tr	0.006	tr				
268	unknown, 73 bp		0.050		0.021	tr				
269	unknown, 96 bp		0.026	0.014						
270	unknown, 246 MW, 103 bp								0.021	
271	unknown, 222 MW, 43 bp, unsaturated alcohol or acid (possibly tetradecatrienoic acid)					1.100		0.047		1.412
272	unknown, 224 MW, 43 bp, unsaturated alcohol or acid (possibly tetradecadienoic acid)			0.298		0.513		0.008		0.239
273	unknown 234 MW unsaturated alcohol or acid, 67 bp					0.252		0.015		0.256
274	unknown							0.008		
275	unknown 236 MW, 41 bp					0.016				tr
276	unknown 238 MW, 79 bp					0.090				0.148
277	2-hexadecanone			0.115		0.056		0.045		0.107
278	unknown unsaturated alcohol							0.698		0.137
279	unknown, 250 MW, 115 bp		tr		tr	0.079	0.021	0.019	0.026	0.026
280	unknown, long-chain polyisoprenoid type compound			0.088		0.007				
281	unknown, 250 MW							0.018		
282	2-heptadecanone (branched)							0.034		
283	unknown, 246 MW, 43 bp							0.057		
284	2-heptadecanone							0.030		
285	hexadecanoic acid (palmitic acid)							0.028		
286	unknown 272 MW polyisoprenoid type compound							0.160		

[a] Compounds identified for the first time in hops are indicated with an asterisk (*). Two asterisks (**) indicate compounds coeluting with internal standard. [b] Direct thermal desorption data. [c] Value reported is the average of four replicate analyses. [d] Steam distillation−extraction data. [e] Compounds for which relative percentages are reported as traces were not integrated by GC. [f] bp stands for base peak. [g] CAS Registry No. was supplied by the author.

Table 2. Essential Oil Content of Selected Hops As Determined by DTD and SDE

hop cultivar	essential oil content (%)	
	DTD[a]	SDE
Nugget	1.73 ± 0.09	1.18
Galena	1.61 ± 0.19	1.07
Willamette	1.15 ± 0.11	0.59
Cluster	0.90 ± 0.09	0.52

[a] Average and standard deviation of four replicate analyses.

soluble to be recovered by SDE, and that is probably the case with formic and acetic acid.

There are 5 unknown compounds that have been found only in DTD data and 30 unknown compounds reported only in SDE data. The compounds found in DTD data are present in very small amounts. The compounds found in SDE data only are mainly long-chain alcohols and acids and unknown terpene esters. We assume that these compounds are artifacts formed during the distillation due to hydrolysis.

Nugget Hops. A total of 150 volatile compounds have been identified for Nugget hops by DTD-GC-MS. The presence and amounts of key oil components used for varietal characterization, as well as their ratios, when compared to the key published by Kenny (1990) and Peacock and McCarty (1992), are typical for the Nugget variety.

It has been observed that Nugget can be distinguished from the other three varieties analyzed by the presence of secondary alcohols (2-nonanol, 2-decanol, 2-undecanol, and 2-dodecanol) that have been shown to be unique for Nugget hops. The presence of 2-nonanol has been used in the varietal key published by Peacock and McCarty (1992). In addition, of four varieties analyzed, sesquiterpene germacrene D was found only in Nugget. Together with Galena, this variety differs from Willamette and Cluster hops by the presence of methyl-3,6-dodecadienoate.

Methyl dodecadienoate has already been used as a key compound for varietal characterization by Peacock and McCarty (1992).

Galena Hops. One hundred and fifty volatile compounds have been found in Galena hops when analyzed by DTD-GC-MS. When results of the analysis are

Table 3. Reproducibility of DTD in Determining Ratios of Oil Components Useful for Varietal Characterization

hop cultivar	ratio[a]									
	M/C		H/C		S/C		H/F		C/Y	
	DTD[b]	SDE[c]	DTD	SDE	DTD	SDE	DTD	SDE	DTD	SDE
Nugget	1.96 ± 0.12	2.08	2.03 ± 0.01	1.86	0.11 ± 0.00	0.13	2378.51 ± 810.68	468.02	174.98 ± 12.66	146.87
Galena	2.67 ± 0.31	2.98	1.85 ± 0.01	1.85[d]	0.13 ± 0.00	*e*	1434.79 ± 434.61	129.81	188.70 ± 6.17	*f*
Willamette	2.02 ± 0.22	2.57	2.55 ± 0.02	2.78	0.04 ± 0.00	0.02	11.30 ± 1.09	33.94	171.86 ± 8.35	*g*
Cluster	4.45 ± 0.39	7.16	2.10 ± 0.01	2.20[d]	0.09 ± 0.00	0.09	*h*	*h*	159.07 ± 12.67	*g*

[a] Abbreviations: M, myrcene; C, caryophyllene; H, humulene; F, β-farnesene; Y, α-ylangene; S, β-selinene. [b] Average and standard deviation of four replicate analyses. [c] Hop oil from SDE. [d] Humulene coeluting with two sesquiterpenes. [e] β-Selinene coeluting with methyl 3,6-dodecadienoate. [f] α-Ylangene coeluting with 2-dodecanone and decanoic acid (branched). [g] α-Ylangene coeluting with 2-dodecanone. [h] β-Farnesene is present in traces.

applied to the keys for varietal characterization published by Kenny (1990) and Peacock and McCarty (1992), they were shown to be characteristic for this variety.

Galena hops has shown to be rich in esters. The relative percentages of methyl 6-methylheptanoate and monoterpene β-ocimene are shown to be higher in Galena hops than in the other three varieties, and the percentage of methyl decanoate was higher in Galena than in Nugget and Willamette varieties. The ester methyl 3,6-dodecadienoate is reported in Galena and Nugget but not in Willamette and Cluster varieties. Another ester, octyl propanoate, is found in Galena and Willamette but not in Nugget and Cluster varieties.

Willamette Hops. In the Willamette hop variety, 144 volatile compounds were reported by DTD-GC-MS. The presence and amounts of key oil components, as well as their ratios, are seen to be characteristic of Willamette on the basis of the keys of Kenny (1990) and Peacock and McCarty (1992).

Willamette is characterized as a high-farnesene hop variety, and our results show a high amount of farnesene present in the Willamette sample. Because the other three varieties analyzed are low-farnesene hops, Willamette can be easily distinguished from the others just by the amount of farnesene present. In addition, it has been observed that Willamette hops have a higher percentage of methyl geranate than other varieties analyzed. Willamette hops have been shown to be the only variety in which ethyl heptanoate and sesquiterpene α-bergamotene were found. Together with Galena, this variety differs from Nugget and Cluster hops by the presence of octyl propanoate.

Cluster Hops. A total of 151 volatile compounds were identified by DTD-GC-MS for Cluster hops. When the data were used to follow the key for varietal characterization of Kenny (1990), they were in good agreement with the characteristics of the Cluster variety.

Among the varieties analyzed, Cluster hops have been shown to have a greater amount of isobutyl isobutyrate and geraniol in relation to the other three varieties, as well as a high amount of β-myrcene and peak 135 (as referred to Table 1) with a retention index of 1296 (an unknown lactone). On the other hand, the relative percentage of sesquiterpene cadinene has been shown to be smaller in Cluster when compared to other varieties analyzed. The ester 2-methylheptyl propanoate, although present in other varieties, was not found in Cluster hops.

As mentioned above and shown in Table 2, hop oil content was higher when determined by DTD-GC-FID. However, the trends are in agreement with the SDE results in which the amount of essential oil is highest in Nugget, followed by Galena, Willamette, and Cluster hops in that order.

The higher essential oil content observed for DTD-GC-FID can be accounted for by minimal losses during the sample preparation, which in the case of SDE could be significant due to evaporative loss during sample concentration steps or incomplete extraction. Sensory evaluation of distillation pot residues from SDE indicated aroma still to be present, suggesting nonquantitative recovery of hop oil by SDE. In contrast, the residue in the desorption tube was odorless, suggesting that quantitative recovery occurred.

There is also a difference in the temperature used for DTD (150 °C) versus SDE (100 °C), which may have contributed to the difference in the essential oil yields for these two methods. Although the higher temperature used in DTD analysis raises the possibility that degradation of some nonvolatile hop constituents may yield volatile compounds that could appear among hop volatiles, it should be noted that the desorption time (at which sample and adsorbent were exposed to high temperature) was only 5 min, and the analysis was performed in an inert atmosphere, which excludes oxidation and hydrolysis reactions. Moreover, except for 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one, which is known to be a product of dehydration and thermal degradation of sugar, no known degradation products of hop constituents were found, and five unknown compounds found only in DTD data were present in very small amounts.

The possibility that compounds present only in DTD data come from Tenax TA was excluded because analysis of desorption tubes filled with Tenax TA and conditioned at 320 °C showed no volatiles present.

As seen from Table 3, the ratios of key oil compounds determined by DTD-GC-FID were mostly in reasonable agreement with those determined by SDE-GC-FID. In the case of the H/F ratio, the difference was greater, but for the purpose of varietal characterization is not significant because the H/F ratio of 3 is used in the key of Kenny (1990). Ratios determined by DTD-GC-FID are shown to be typical for the varieties analyzed. As seen from the table, the DTD-GC-FID method has shown high reproducibility in determination of ratios of oil components useful for varietal characterization.

CONCLUSION

When used for essential oil profiling of hops, the DTD method has proven to be as sensitive as the conventional SDE method. The data obtained by DTD-GC-MS have proven to be in generally good agreement with SDE data and with the literature data for the varieties analyzed. By analyzing other hop varieties, the DTD method can be used to create a database useful for the confirmation of hop variety identities. Due to the minimal losses during the sample preparation, DTD has a higher essential oil yield than conventional SDE. The DTD-GC has also been shown to be highly reproducible in determination of ratios of key oil components used for varietal characterization of hops. The ratios were in generally good agreement with the SDE data and typical for the varieties analyzed. DTD can, therefore, be used successfully for varietal characterization of hops for the varieties analyzed.

In addition to the significant time saving that DTD offers (the time needed for sample preparation prior to GC-MS profiling of hops was ~20 min as compared to 6 h in the case of conventional SDE), DTD has other advantages over methods for essential oil analysis of hops that are currently in use. First, the method requires only ~1 g of hop sample, which economizes storage space, reduces the time needed for sample preparation, and, more important, makes the method suitable for the analysis of individual cones in cases when identification of hop mixtures is needed. Second, the method does not require use of solvent, so the solvent exposure, as compared to the other methods, is significantly reduced. Third, the method does not require elaborate procedures. The thermal desorber apparatus is easy to operate, and sample cleaning is reduced to a minimum. Its labor and time efficiencies

make DTD a method that can significantly increase the number of hop samples that can be analyzed daily in the laboratory. For research purposes, the method can be of great significance for studies involving the analysis of large numbers of hop samples.

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LITERATURE CITED

Buttery, R. G.; Ling, L. C. Identification of hop varieties by gas chromatographic analysis of their essential oils. *J. Agric. Food Chem*. **1967**, *15*, 531−535.

Grant, H. L. Hops. In *Handbook of Brewing*; Hardwick, W. A., Ed.; Dekker: New York, 1995.

Green, C. P. Use of chromatography data to identify varieties in binary mixtures of hops. *J. Inst. Brew*. **1997**, *103*, 293−296.

Green, C. P.; Osborne, P. Rapid method for obtaining essential oil from hops. *J. Inst. Brew*. **1993**, *99*, 335−339.

Grimm, C. C.; Lloyd, S. W.; Miller, J. A.; Spanier, A. M. The analysis of food volatiles using direct thermal desorption. In *Techniques for Analyzing Food Aroma*; Marsili, R., Ed.; Dekker: New York, 1998.

Hartman, T. G.; Overton, S. V.; Manura, J. J.; Baker, C. W.; Manos, J. N. Short path thermal desorption: Food science applications. *Food Technol.* **1991**, *45*, 104−105.

Hartman, T. G.; Karmas, K.; Chen, J.; Shevade, A.; Deagro, M.; Hwang, H. I. Determination of vanillin, other phenolic compounds and flavors in vanilla beans by direct thermal desorption-gas chromatography and gas chromatography−mass spectrometry analysis. In *Phenolic Compounds in Food and Their Effects on Health*; ACS Symposium Series 506; Ho, C.-T., Lee, C. Y., Huang, M.-T., Eds.; American Chemical Society: Washington, DC, 1992.

Jennings, W.; Shibamoto, T. *Qualitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography*; Academic Press: New York, 1980; pp 58−87.

Katsiotis, S. T.; Langezaal, C. R.; Schefer, J. J. C.; Verpoorte, R. Comparative study of the essential oils from hops of various *Humulus lupulus* L. cultivars. *Flavour Fragrance J*. **1989**, *4*, 187−191.

Kenny, S. T. Identification of US-grown hop cultivars by hop acid and essential oil analysis. *J. Am. Soc. Brew. Chem*. **1990**, *48*, 3−8.

Lam, K. C.; Nickerson, G. B.; Deinzer, M. A rapid solvent extraction method for hop essential oils. *J. Agric. Food Chem*. **1986**, *34*, 63−66.

Langezaal, C. R.; Chandra, A.; Katsiotis, S. T.; Scheffer, J. J. C.; De Haans, A. B. Analysis of supercritical carbon dioxide extracts from cones and leaves of a *Humulus lupulus* L. cultivar. *J. Sci. Food Agric.* **1990**, *53*, 455−463.

Likens, S. T.; Nickerson, G. B. Identification of hop varieties by gas chromatographic analysis of their essential oils. *J. Agric. Food Chem*. **1967**, *15*, 525−530.

Maarse, H.; Visscher, C. A. Hop oil. In *Volatile Compounds in Food*; Maarse, H., Visscher C. A., Eds.; TNO−CIVO Food Analysis Institute: Utrechtseweg, The Netherlands, 1989.

Majlat, P.; Erdos, Z.; Takacs, J. Calculation and application of retention indices in programmed temperature gas chromatography. *J. Chromatogr.* **1974**, *91*, 89−110.

Manura, J. J.; Hartman, T. G. Application of a short-path thermal desorption GC accessory. *Am. Lab.* **1992**, *5*, 46−52.

Nickerson, G. B.; Likens, S. T. Gas chromatographic evidence for the occurrence of hop oil components in beer. J. *Chromatogr.* **1966**, *21*, 1−5.

Peacock, V. E.; McCarty P. Varietal identification of hops and hop pellets. *MBAA Tech. Q.* **1992**, *29*, 81−85.

Peppard, T. L.; Ramus, S. A.; Witt, C. A.; Siebert, K. J. Corelation of sensory and instrumental data in elucidating the effect of varietal differences on hop flavor in beer. *J. Am. Soc. Brew. Chem*. **1988**, *47*, 18−26.

Perpette, P. Varietal discrimination of hop pellets by essential oil analysis I. Comparison of fresh samples. *J. Am. Soc. Brew. Chem*. **1998**, *56*, 104−108.

Pickett, J. A.; Coates, J.; Sharpe, F. R. Distortion of essential oil composition during isolation by steam distillation. *Chem. Ind*. **1975**, *13*, 571−572.

Pickett, J. A.; Sharpe, F. R.; Peppard, T. L. Aerial oxidation of humulene. *Chem. Ind*. **1977**, *1*, 30−31.

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