Chemistry of Hop Aroma in Beer[1]

Val E. Peacock[2] and Max L. Deinzer, *Department of Agricultural Chemistry, Oregon State University, Corvallis 97331*

ABSTRACT

Three beers were analyzed by gas chromatography/mass spectrometry for hop-derived flavor components. Hop ether, karahana ether, linalool, geraniol, humulol, humuladienone, humulenol II, and humulene epoxides I, II, and III are among the compounds identified in beer that are believed to influence beer flavor. These humulene oxidation products probably contribute to the traditional "kettle-hop" flavor/aroma of beer, but geraniol and linalool contribute to a floral flavor note that is distinctly different from the kettle-hop aroma/taste. The humulene oxidation products, the main one of which is humulene epoxide II, increased in concentration with hop storage.

Key words: *Aroma, Beer, Geraniol, Hops, Humulene, Linalool, Taste*

The major components of hop oil, terpene and sesquiterpene hydrocarbons, are rarely found in beer (9,13) and are not considered responsible for hoppy flavors in beer. However, the oxidation products of these hydrocarbons, which make up 5–10% of typical hop oil, *are* commonly found in beer and are therefore much more likely to be responsible for hoppy flavors.

Oxidation products of humulene, one of the major sesquiterpene hydrocarbons, have been the focus of much attention in recent years as a possible source of the traditional "noble-hop" or "kettle-hop" aroma of beers brewed with "aroma hops." These compounds are in much higher concentration in the humulene-rich traditional "aroma" varieties than in other hops (6). Also, these compounds are formed by oxidation of humulene during hop storage (14), which may be related to the fact that aging of hops before use improves hop aroma properties.

The earliest mention of humulene oxidation products in beer was by Shimazu et al (12) in 1974. They found humuladienone in a variety of beers at levels of 34–72 μg/L and reported a sensory threshold of 100 μg/L for the compound. Sandra and Verzele (11) reported looking for humuladienone in beer and finding none. They claimed to have a sensitivity limit of 1 μg/L. Tressl et al (13) reported a humuladienone level of 10 μg/L in beer.

Both Tressl et al (13) and Peacock et al (9) reported relatively large amounts of other humulene oxidation products as well as many other hop-derived compounds in beer. Tressl et al (13) reported humulenol II at a concentration of 1,150 μg/L, and Peacock et al, who found it at 250–500 μg/L, speculated that it is a hop flavor contributor with a sensory threshold of 500 μg/L (9). Tressl et al (13) reported large amounts of humulol (220 μg/L) and humulene epoxide I (125 μg/L) and a lesser amount (40 μg/L) of humulene epoxide II in a "hoppy" German beer. Peacock et al (9) found lesser amounts of humulol and humulene epoxide I in various American beers and noted that the beers brewed with the traditional "aroma" varieties contained much more of these compounds (especially humulenol II) than the beers brewed with other hops.

Tressl et al[3] put more emphasis on the flavor of the hop-derived carotenoids β-damascenone and β-ionone, which they found in beer at 30 and 3 μg/L, respectively. They reported their sensory thresholds in *water* to be 0.009 and 0.007 μg/L, respectively. Meilgaard (3) reported the threshold of β-ionone to be 1.3 μg/L in beer, so these carotenoids may well have an effect on beer flavor. Tressl et al also speculated that the bicyclic terpenoids hop ether and karahana ether may play a part in beer hop flavor. They reported 35 and 60 μg/L, respectively, of these compounds in beer[3] and 5 μg/L thresholds for both compounds in water.

Linalool has been found in beer by Micketts and Lindsay (5), Tressl et al (13), and Peacock et al (9). All three groups have speculated that it may be a flavor contributor to beer. Peacock et al (8) found large amounts of geraniol and geranyl isobutyrate in some beers and claimed that these compounds, with linalool, are responsible for a floral flavor note in these beers.

[1]Presented at the 47th Annual Meeting, Miami, FL, May 1981.

[2]Present address: Philip Morris Research Center, Beverage Products Research and Development, P.O. Box 26583, Richmond, VA 23261.

[3]R. Tressl, F. Fendesack, and H. Köppler. Paper presented at ASBC 45th Annual Meeting, Portland, OR, April 1979.

0361-0470/81/04013606/$03.00/0

EXPERIMENTAL

Beer Analyses

The three beers were a commercial Austrian beer, a premium American beer, and a pilot brew prepared by a commercial American brewer.

The following basic work-up procedure was used for all three beers. Two liters of beer was mixed with 2 kg of Celite 545 until the entire mass had a powdery consistency. The beer-saturated Celite was placed in a large (13 × 40-cm) liquid chromatography (LC) column. (Only a third of the Celite mixture could fit in the column at one time.) Each of the thirds of Celite was eluted with 2 L of freshly distilled methylene chloride, using a total of 6 L. The eluent was dried over anhydrous sodium sulfate and reduced in volume at reduced pressure to a mass of about 0.5 g. This residue contained a large percent of free fatty acids and phenolic compounds (maltol and isomaltol) that interfered with the gas chromatography (GC) analysis. The following procedures were used to clean up the sample and quantify the volatiles of interest.

Beer 1. The residue was dissolved in 150 ml of ether and extracted twice with 150 ml of 10% Na_2CO_3. The ether was then dried over anhydrous $MgSO_4$ and reduced in volume at reduced pressure to a mass of about 1 g. This sample was further concentrated under a stream of N_2 until it no longer smelled of ether (about 10 min). The remaining material was weighed (0.158 g). One microliter of this sample was injected into the gas chromatograph and all the resulting peaks were quantified. Assuming that 100% of the sample was detected by the instrument, each compound was quantified by multiplying the mass of the entire sample (0.158 g) by the area of its peak in the chromatogram and dividing by the sum of the peak areas of the entire sample. Some nonvolatile residue remained in the injection port of the gas chromatograph, which would cause some error in these calculations.

Beer 2. This sample was analyzed identically to beer 1 except that it was extracted with 10% NaOH instead of with Na_2CO_3. The sample residue had a mass of 0.090 g.

Beer 3. Before beer 3 was analyzed, 1.0 ml of 0.1% naphthalene in 100% ethanol was pipetted into the 2 L of beer, resulting in a 500 μg/L concentration of the compound as a standard. The Celite procedure was followed as usual. The resulting residue was cleaned up by the following procedure. An LC column (2.5 cm i.d.) was filled with 25 cm of Fischer adsorption alumina, then 2.5 cm of Na_2CO_3, and then 2.5 cm of anhydrous Na_2SO_4. The column was wetted with hexane and the sample poured onto the top of the column. The column was eluted with 100 ml of hexane and then 200 ml of ether. The combined hexane and ether fractions were reduced in volume at reduced pressure to 0.1–0.2 ml and analyzed by GC and GC/mass spectrometry (MS) as such. The compounds reported were quantified by direct comparison with the naphthalene standard. This avoided the previous problem of the

entire sample not being volatile. Since the sample was not fractionated by LC before the GC analysis, another problem of quantification was avoided, ie, not having the standard in the same LC fraction as the compound in question. This problem casts serious doubts on the previously reported results of both Peacock et al (9) and Tressl et al (13).

Hop Oil Analyses

Hop oils were isolated and analyzed by previously published methods (8).

Humulene and Caryophyllene Oxidations

Both compounds were purified by LC on an alumina column (eluting with hexane) to remove any oxidation products. A few percent of some other hydrocarbons were present in each sample (calamenene in the humulene and humulene in the caryophyllene), but these were ignored in the experiment. All of the products derived from humulene and caryophyllene were quantified by GC and identified by MS. The data was normalized to present the relative amounts of the compounds. The only experiments in which this changed the raw data substantially were in the fermentations. Therefore, all the fermentation products were ignored.

Boiled 1.5 hr. Fifty microliters of humulene or caryophyllene were refluxed in 200 ml of distilled water for 1.5 hr. None of the volatiles were allowed to escape. The mixture was cooled and extracted with ether. The ether was dried over anhydrous Na_2SO_4 and reduced in volume at reduced pressure to a volume of 0.5 ml. This sample was analyzed by GC and GC/MS directly.

Boiled 1.5 hr at pH 4.4. This was done exactly as above using 0.1*M* KH_2PO_4 instead of water.

Boiled 24 hr. This sample was handled exactly as the 1.5-hr water boil except that it was boiled for 24 hr.

Fermentations. Fifty microliters of humulene or caryophyllene was added to 1L of 6% glucose solution with 1 g of commercial yeast nutrient and 0.05 g of commercial brewer's yeast. The mixture was fitted with a fermentation lock to release CO_2 but prevent air from entering. The fermentation was allowed to sit at room temperature for four weeks. The mixture was then worked up and analyzed as above.

Photolysis. Forty microliters of humulene was dissolved in 40 ml of acetone and 10 ml of water and photolyzed under a mercury ultraviolet lamp for 89 hr. The acetone was removed at reduced pressure, and the remaining water was extracted with ether. From this point, the sample was analyzed as above.

GC

A fused silica column (0.2 mm × 50 m) coated with Carbowax 20M was used in the GC analyses. The column was temperature programmed to go from 60 to 190° C at 4° C/min and then hold at 190° C for 30 min. Helium was the carrier gas. A Hewlett Packard model 5830GC with a model 18835B capillary inlet system was used with a flame ionization detector in conjunction with a Hewlett Packard model 18850A GC terminal for data reduction and peak quantification.

GC/MS

All peaks reported were identified by GC/MS, using the above GC conditions. Mass spectral data were acquired on a Finnigan 4320 quadrapole mass spectrometer.

Humulene Epoxides

The mixture of humulene epoxides was prepared by the method of Damodaran and Dev (2),[4] using *m*-chloroperbenzoic acid instead of perbenzoic acid. The mixture was analyzed by GC/MS.

[4]The original paper does not report formation of humulene epoxide III, only humulene epoxides I and II and humulene diepoxide.

Threshold Determinations

These were conducted using the Ascending Method of Limits Test (4) with a commercial American beer.

RESULTS AND DISCUSSION

Table I shows the analysis of three beers for hop-derived flavor components and gives available threshold data on these compounds.

Peacock et al (8) previously reported finding approximately a 200 μg/L level of linalool in a very floral-flavored beer. Tressl et al (13) reported a 470-μg/L level of linalool in beer. Threshold data on linalool (3,8) indicate that 200 or 470 μg/L-levels of linalool in beer would be an overpowering flavor. The 34 μg/L reported by Micketts and Lindsay in a commercial American beer (5) and the 15–44 μg/L reported here are much more reasonable estimates of the amount of this compound in beer. The 5–69 μg/L geraniol concentration reported here is much more realistic than the 200 μg/L reported earlier (8); a geraniol level of 200 μg/L was quite overpowering to our taste panel.

Beer 3 of Table I was judged to be quite floral by our taste panel. The threshold data presented in the table indicate that linalool and geraniol are in sufficient concentration to be responsible for this flavor note. Geranyl isobutyrate, although insufficient in concentration to be flavor-active in beer 3, is in much higher concentration (reported at 200 μg/L [8]) in other beers and probably has some minor sensory contribution to this flavor note.

Hop and karahana ethers, speculated to be hop flavor contributors in beer,[5] are in too low a concentration in the beers reported in Table I to be of significance.

The amounts of humulenol II in the beers reported in Table I are well below the amounts previously reported in beer (9,13) and well below its reported threshold. We reevaluated its previously reported threshold (500 μg/L) in beer (9) and determined that this figure was too low. A much more realistic threshold for this compound is 2,500 μg/L, although it can be detected at much lower concentrations by many individuals.

The humulene epoxides are probably of greater importance to beer flavor. Tressl et al[5] reported a threshold of 10 μg/L for humulene epoxide I in *water*. We have done preliminary threshold work on humulene epoxide II in beer and currently estimate its threshold to be 450 μg/L. This is in close agreement with the estimate of the flavor panel of an independent American brewery.[6] The sample of humulene epoxide II used in both tests was a mixture containing about 65% humulene epoxide II, 15% humulene epoxide I, and 10% each of humulene epoxide III and humulene diepoxide. Judging by the data of Table I, this is a reasonable approximation of the humulene epoxides found in fresh beer. (Humulene epoxide II rearranges to humulenol II under acidic conditions [2]; this is probably why it is seldom found in beer in large concentrations; it rearranges slowly at the pH of beer. Freshly brewed beer would probably have much more humulene epoxide II than older beer. This rearrangement may also take place in the work-up procedures used to analyze beer, thus complicating the results.) Apparently these humulene epoxides, collectively or singly, may contribute to the flavor of beer.

The contributions of humulol and humuladienone in beer are not conclusively established. Apparently a beer must be quite heavily hopped before these humulene oxidation products would be more than mildly flavor-active.

Changes in Hop Oil During Storage and Brewing

Table II gives the yield of selected hop oil components of six different hop varieties before and after a one-year storage period. In general, the hydrocarbons (especially myrcene) disappear and oxidation products of humulene increase in concentration. The

[5]Refer to footnote 3.

[6]Unpublished data.

varieties in which α-acids decrease most also show the most humulene oxidation. Also worth noting is that, with storage, geranyl isobutyrate is hydrolyzed to its much more flavor-active alcohol, geraniol.

Shimazu et al (12) reported that the concentration of humuladienone in hops increased with storage and that pure humulene, upon standing for several days, formed substantial amounts of humuladienone. They also state that this transformation was accelerated by temperature and sunlight. Pickett et al (10), on the other hand, found that humulene epoxide II is by far the major thermal oxidation and photooxidation product of humulene under a variety of conditions and that no detectable humuladienone is formed even after 33% of the humulene is converted to the epoxide II. Pickett et al did report small amounts of humulenol II after such extreme oxidation. Traces of humulene epoxide I, humulenol I, humulol, and humulene diepoxide were also reported.

The hop storage data of Table II is in better agreement with the findings of Pickett et al (10) than with those of Shimazu et al (12); the main humulene oxidation product formed during storage was humulene epoxide II, not humuladienone. The data of Table III also support the claims of Pickett et al. Here too, the main oxidation product formed under a number of conditions was humulene epoxide II. Humuladienone was not detected in any of

Table I.
Hop Oil Components in Beer (μg/L)

Compound	Beer 1[a]	Beer 2[b]	Beer 3[c]	Maximum Level Previously Reported in Beer	Threshold in Beer
Humulene	27	...	...	...	...
Caryophyllene	75	...	...	...	...
Hop ether	...	...	3	35[d]	5 in water[e]
Karahana ether	...	...	3	60	5 in water[e]
Linalool	25	15	44	470,[d] 200[f]	27[f]
Geraniol	5	...	69	200[f]	36[f]
Geranyl isobutyrate	...	...	5	150[f]	450[f]
Geranyl acetate	...	...	10	...	
α-Terpineol	...	120	19	...	2,000[g]
Humuladienone	...	...	2	72,[h] 10[d]	100[h]
Humulene epoxide I	...	75	10	125[d]	10 in water[e]
Humulene epoxide II	75	250	11	40[d]	(450)[i]
Humulene epoxide III[i]	20	...	...	...	...
Caryolan-1-ol	...	...	8	...	...
Humulol	75	90	10	220[d]	...
Humulenol II	225	180	72	1,150[d]	2,500[j]
β-Eudesmol	75	...	...	...	...

[a]Commercial Austrian beer.
[b]Commercial American beer, premium.
[c]Pilot brew made by a commercial American brewer.
[d]From Tressl et al (13).
[e]From Tressl et al (14).
[e]From paper by R. Tressl, F. Fendesack, and H. Köppler, presented at ASBC 45th Annual Meeting, Portland, OR, April 1979.
[f]From Peacock et al (8).
[g]From Meilgaard (3).
[h]From Shimazu et al (12).
[i]Tentatively identified.
[j]Reported previously (9) as 500 μg/L.

Table II
Changes in Oil Components During Hop Storage[a]

	Hop Variety and Year of Test[b]											
	Hallertauer		Perle		Hersbrucker		Tettnanger		Cascade		Cluster	
Compound	1980	1981	1980	1981	1980	1981	1980	1981	1980	1981	1980	1981
Myrcene	92.1	78.6	119	35.0	62.4	53.8	239	4.90	329	7.04	218	59.8
Linalool	3.08	2.90	2.08	0.94	3.75	4.10	7.50	3.82	6.02	3.60	2.42	2.16
Geraniol	...	...	...	...	...	...	0.30	1.99	1.89	3.52	1.32	1.03
Geranyl isobutyrate	...	...	...	...	...	...	1.20		10.9	15.2	3.30	0.24
Hop ether	0.15	0.20	0.08	0.07	0.15	0.40	0.05	0.03	0.21	0.40	0.06	0.09
Karahana ether	0.15	0.20	0.08	0.07	0.15	0.50	0.05	0.04	0.28	0.40	0.11	0.09
Humulene	350	469[c]	391	355	219	207	416	461	122	107	110	154
Humulene epoxide I	3.06	7.70	1.84	8.28	2.63	12.8	0.50	4.57	0.56	7.60	0.66	2.63
Humulene epoxide II	10.05	28.0	6.56	30.6	7.50	38.4	3.80	16.35	3.85	33.2	0.99	6.63
Humuladienone	0.60	1.30	0.64	2.09	0.53	2.30	0.30	0.42	0.14	2.24	...	.01
Humulol	1.05	3.00	0.72	1.08	0.38	3.30	1.10	2.08	0.21	0.56	0.88	2.02
Percent α-acids	7.7	6.2	7.7	6.2	7.4	4.7	6.3	5.4	7.6	4.6	12.3	11.0

[a]Concentrated pellets; values are reported as milligrams per 100 g of hops.
[b]Samples stored refrigerated for one year.
[c]Calculations were done by multiplying the percent of the compound in the oil by the yield of the oil from the hops, divided by the mass of the hops from which the oil was isolated. The small sample size of the hops resulted in a small amount of oil, which has caused some error in the calculations, ie, the amount of humulene in the hops is believed not to increase.

TABLE III
Influence of Various Treatments on the Production (%) of Oxidation Products from Some Hop Oil Components

Compounds	Treatment				
	Boiled				
	1.5 hr in Water	1.5 hr at pH 4.4	24 hr in Water	Fermented	Photolyzed
From humulene oxidation					
Humulene (retained)	99.90	98.82	85.24	92.64	89.42
Humulene epoxide I	···	0.12	2.35	0.37	0.36
Humulene epoxide II	0.10	0.67	6.02	0.74	8.12
Humulene epoxide III[a]	····	0.15	2.74	0.19	0.75
Humuladienone	···	···	0.25	···	···
Humulol	···	0.24	0.98	2.89	···
Humulenol II	···	···	2.42	3.17	1.35
From caryophyllene oxidation					
Caryophyllene (retained)	···	93.85	99.41	···	···
Caryophyllene oxide	···	6.07	0.58	···	···
Caryolan-1-ol	···	0.08	0.01	···	···

[a]Tentatively identified.

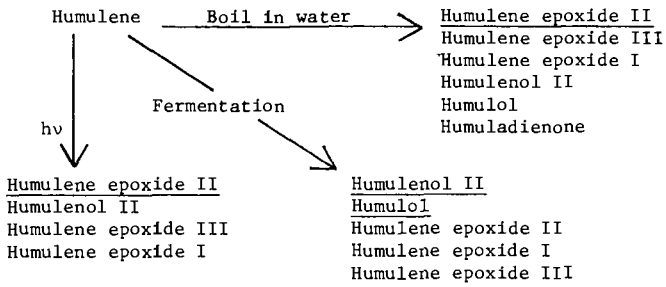

Fig. 1. Oxidation pathways of humulene.

the oxidized samples except when the compound was boiled for 24 hr in water; then a small amount of the compound was found. Simulated wort boiling (1.5 hr) produced only very small amounts of humulene epoxide II; the boiling time is too short to produce much oxidation. Results of the various oxidation methods are shown graphically in Fig. 1.

The structures and mass spectra of the humulene oxidation products are presented in Figs. 2–4. The mass spectra of humuladienone and humulene epoxide II are quite similar. This may be why conflicting reports are given about these two compounds.

In Tables I and III, humulene epoxide III is reported. This compound has not been mentioned in the literature before. It has been tentatively identified by the following evidence. 1) It is one of four compounds formed by the epoxidation of humulene with *m*-chloroperbenzoic acid. The other three are humulene diepoxide and humulene epoxides I and II. 2) The GC retention time of the compound is very similar to that of the other two humulene epoxides on Carbowax 20M and is quite difficult to resolve from that of humulene epoxide II. 3) The infrared spectrum of a strongly concentrated sample of the mixture of products from the epoxidation reaction shows no hydroxyl or carbonyl absorption. 4) The mass spectrum of the compound shows a molecular ion at m/z = 220. A sample of this compound has not yet been isolated in pure form. Hence, no nuclear magnetic resonance or infrared data are available for a structure proof at this time.

Table III also contains some oxidation data on caryophyllene, the other major sesquiterpene hydrocarbon in hops. Much of the oxide is formed in the pH 4.4 simulated wort boiling but very little in the water (24-hr) boiling. Very little of these caryophyllene oxidation products is found in beer (9,13) so this is probably not significant.

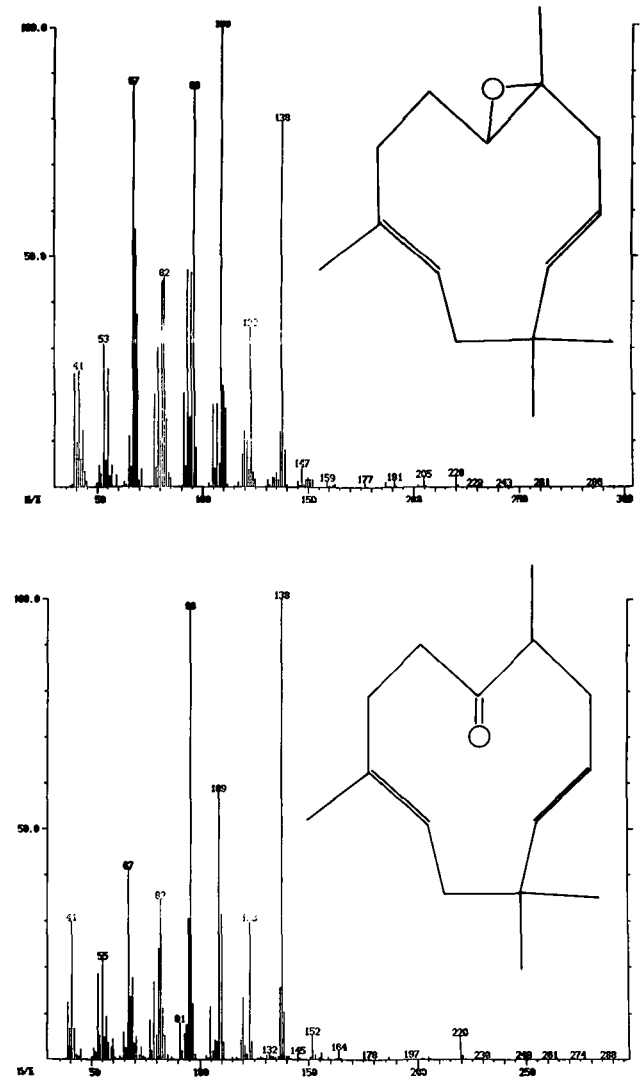

Fig. 2. Mass spectra and structures of humulene oxidation products: **top,** humulene epoxide II; **bottom,** humuladienone.

TABLE IV
Theoretical Maximum Amounts of Hop Oil Components in Beer[a]

Hop Sample[b] and Oxidation Compound	Concentration In Hops (mg/100 g)	Concentration In Beer (μg/L)
Hallertauer 1981		
Humuladionone	1.3	21
Humulene epoxide I	7.7	124
Humulene epoxide II	28.0	451
Humulol	3.0	48
Humulenol II	11.5	185
Cascade 1981		
Linalool	3.6	78
Geraniol	3.5	76
Geranyl isobutyrate	15.2	330
Hop ether	0.4	9
Karahana ether	0.4	9

[a]Calculated using the equation: concentration in beer (μg/L) = [E × (mg/100 g of hops) × IAA]/[U × %AA], where E = percent extraction of hop oil components (assumed 100), IAA = iso-α-acids level (mg/L) in the beer (assumed 25), U = percent utilization of α-acids (assumed 25), and %AA = percent α-acids in the hops: Hallertauer, 6.2; Cascade, 4.6.
[b]Hop samples correspond to those in Table II.

The relevant question about these oxidation products is: how much of them does beer contain and what effect on flavor do they have? An attempt has been made (Table IV) to address this question. We calculated the amount of some of these compounds that should end up in finished beer brewed with the aged Hallertauer hops of Table II to a bitterness level of 25 mg of α-acids per liter. We assumed in the calculations that the efficiency of extraction of the α-acids into the beer was 25% (1) and that the efficiency of extraction of the hop oil components was 100%. The calculations do not include any corrections for the formation of these compounds by the oxidation of humulene during wort boiling and fermentation or for rearrangement of any of these compounds during processing. The theoretical yields of these compounds in beer (Table IV) show a number of interesting results. First, the amount of humulene epoxide II in beer should be much greater than the concentration of humulene epoxide I or humulenol II. The reverse is observed in the previously reported works of both Tressl et al (13) and Peacock et al (9). Both observe large amounts of humulenol II and little or no humulene epoxide II in beer. This would indicate that much of the humulene epoxide II in hops is converted to humulenol II in the beer during brewing or by aging on the shelf. The rearrangement of humulene epoxide II to humulenol II is acid-catalyzed (2,7) and possibly takes place slowly

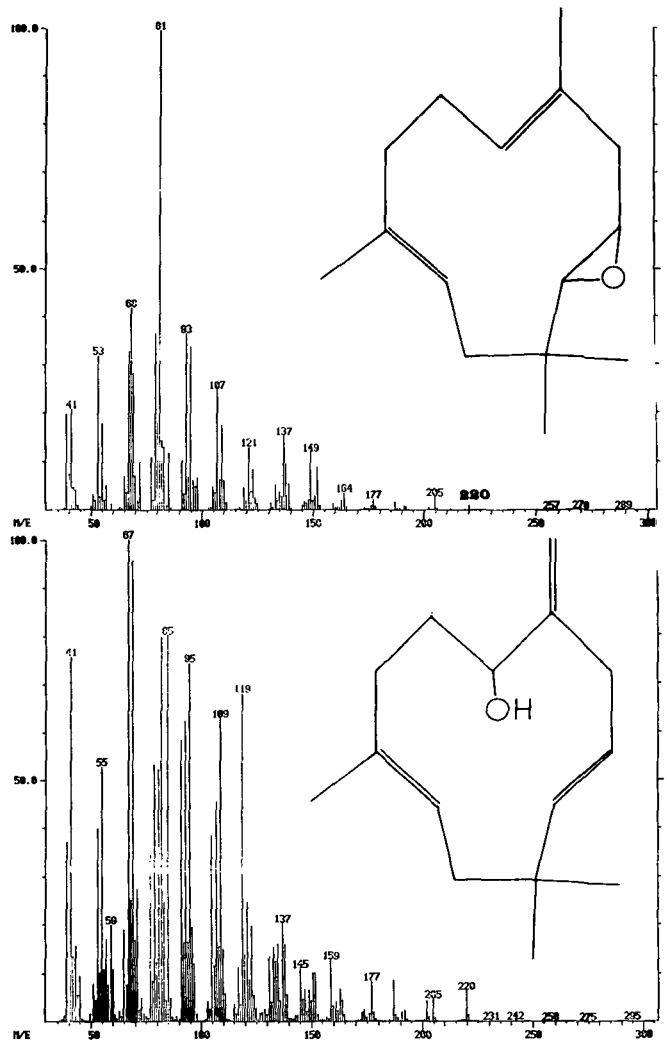

Fig. 3. Mass spectra and structures of humulene oxidation products: **top,** humulene epoxide III (tentatively identified); **bottom,** humulenol II.

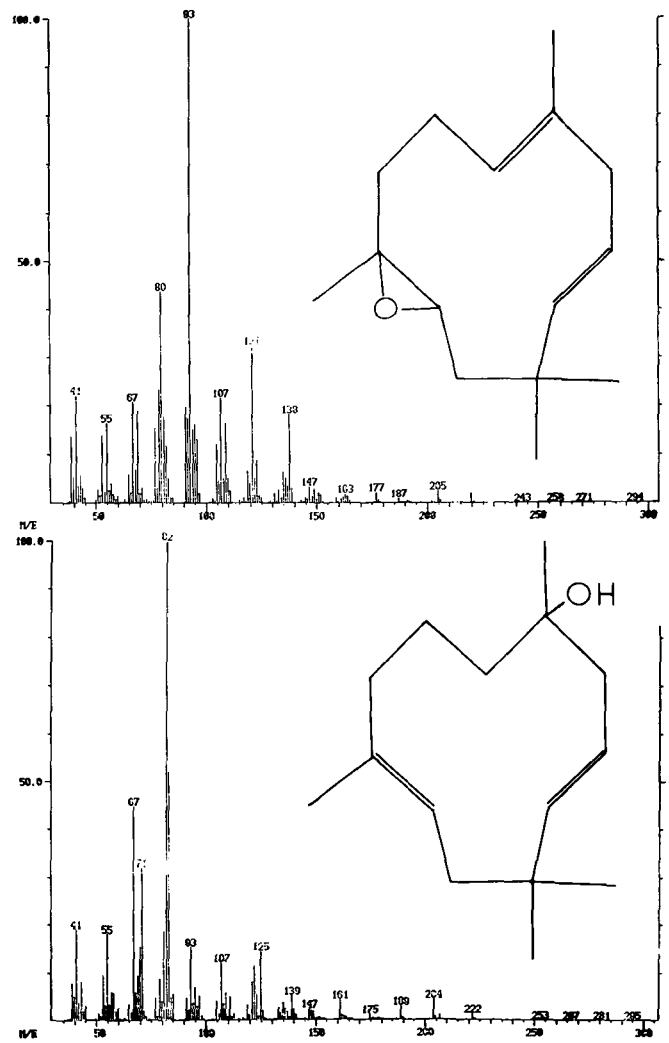

Fig. 4. Mass spectra and structures of humulene oxidation products: **top,** humulene epoxide I; **bottom,** humulol.

as beer is stored. Second, the calculated level of humulene epoxide II (451 μg/L) indicates that in fresh beer this compound may well have an effect on beer flavor. The estimated threshold of 450 μg/L in beer, reported in Table I for the synthetic mixture of humulene epoxides (predominantly humulene epoxide II), supports this hypothesis. Third, at 124 μg/L in beer (Table IV), humulene epoxide I would also be of some importance to hop flavor. From what is now known, these humulene oxidation products are probably important to beer flavor; however their individual contributions are still undetermined.

Also in Table IV are calculations of the theoretical yield of some terpenoids of interest that would be found in beer brewed with the aged Cascade hops of Table II. The same assumptions are made as for the previous calculations. these theoretical yields, except the exaggerated geranyl isobutyrate level, are in close agreement with the data on beer 3 (Table I).

The concentrations of both linalool and geraniol in beer are important. Both are well above their sensory thresholds in some beers and in the calculations of Table IV. Because the levels of geranyl isobutyrate reported in beer are all well below 330 μg/L, much of it is probably lost during brewing. Its main influence on flavor appears to be that, to some extent, it hydrolyzes to geraniol in finished beer (8).

Based on Tressl's[7] reported thresholds of 5 μg/L in *water* for both hop ether and karahana ether, these compounds are probably not major contributors to hop flavor in beer at 3 μg/L.

[7]Refer to footnote 3.

ACKNOWLEDGMENTS

We wish to thank Anheuser-Busch, Inc., The Stroh Brewery Company, and the Hop Research Council for support of this project.

LITERATURE CITED

1. Burgess, A. H. Hops-Botany, Cultivation and Utilization. Interscience Publishers, Inc.: New York, 1964.
2. Damodaran, N. P., and Dev, S. *Tetrahedron* 24:4123, 1968.
3. Meilgaard, M. *Tech. Q. Master Brew. Assoc. Am.* 12:151, 1975.
4. Meilgaard, M. *J. Am. Soc. Brew. Chem.* 38:99, 1980.
5. Micketts, R. J., and Lindsay, R. C. *J. Food Protect.* 41:722, 1978.
6. Naya, Y., and Kotake, M. *Bull. Chem. Soc. Jpn.* 45:2287, 1972.
7. Nigam, I. C., and Levi, L. *J. Org. Chem.* 27:2803, 1964.
8. Peacock, V., Deinzer, M., Likens, S., Nickerson, G., and McGill, L. *J. Agric. Food Chem.* In press, 1981.
9. Peacock, V., Deinzer, M., McGill, L., and Wrolstad, R. *J. Agric. Food Chem.* 28:774, 1980.
10. Pickett, J. A., Sharpe, F. R., and Peppard, T. L. *Chem. Ind. London 1977*, p. 30.
11. Sandra, P., and Verzele, M. *Eur. Brew. Conv., Proc. Congr. 15th, Nice, 1975*, p. 107.
12. Shimazu, T., Hashimoto, N., and Kuroiwa, Y. *Proc. Am. Soc. Brew. Chem.* 33(1):7, 1975.
13. Tressl, R., Friese, L., Fendesack, F., and Köppler, H. *J. Agric. Food Chem.* 26:1422, 1978.
14. Tressl, R., Friese, L., Fendesack, F., and Köppler, H. *J. Agric. Food Chem.* 26:1426, 1978.

[Received May 12, 1981]