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THE EFFECT OF GEOGRAPHICAL SOURCE ON THE VOLATILE OIL OF HOPS.

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Among the many factors which tend to influence the composition of volatile oils, geographical source, with its attending conditions of climate and soil, is of noteworthy importance. It is a generally accepted fact that a close relationship exists between the growth of a plant with the formation of its constituents, and climatic factors such as, heat, light, moisture, dryness and soil conditions. With regard to volatile oils in general, a number of factors may produce variation in aroma or quality. This geographical location may influence the aromatic property of an oil as attested by Jeancard and Satie,[1] who state that the locality in which lavender, thyme, rosemary and roses are grown has considerable effect upon certain constants of the oils. According to Bonnier,[2] altitude, light, hygrometric conditions and temperature also affect the plant functions and thus affect its composition. Condition of the soil is also important according to Lamothe,[3] who states that soil fertilized with superphosphates increases the esters of lavender oil. In experiments with peppermint Charabot and Hebert[4] have shown that soil treated with fertilizers produce plants richer in esters and odor-bearing compounds.

Since the conditions mentioned affect the composition of a number of volatile oils, it may be easily comprehended that similar effects may be produced on hops grown in separate localities under different conditions. Furthermore, since the effects on other oils have been noted chiefly in the esters or odor-bearing constituents, it is very probable that the volatile oil of hops would suffer like changes in ester content. For the purpose of ascertaining the truth of the above assumption the following investigation was undertaken.

In order to determine whether any differences exist in the volatile oils of hops, the physical and chemical constants were carefully determined. The physical properties, specific gravity, optical rotation, refraction, and solubility in alcohol are most important in revealing differences due to variation in composition.

[1] Jeancard, P., and Satie, C. La Chimie des Parfums en 1908. Revue Générale de Chimie pure et appliquee Tome 12, p. 181, 1909.

[2] Bonnier, G., Recherches experimentales sur l'adaption des plantes au climat Alpin. Annales des Sciences Naturelles Botanique. Serie 7, Tome 20, p. 217, 1894.

[3] Lamothe, L., Lavender and its Oil. American Perfumer and Essential Oil Review. Vol. 3, p. 128, 1908.

[4] Charabot, A., and Hebert, A. Bulletin du Jardin Colonial. Vol. 27, 1902, 3rd series, pp. 224-914.

Among the chemical constants the ester value is possibly of the most importance because of its close relationship to the aroma of the oil.

For the purpose of learning whether any constant differences exist in the various hops, it was planned to compare the oils distilled from hops grown in the hop-producing sections of the United States with the oil distilled from an authentic sample of imported hops, all of the samples to be from hops grown during the same season. The sections chosen in the United States were California, Oregon, Washington and New York. The imported hops were from Bohemia.

A comparison of the oils obtained from the hops during a single season would give results which would be valuable in determining differences for that particular season, but it was also important to ascertain whether the same differences occurred from year to year. Therefore the experiments were carried on for several successive seasons and the oils obtained from the hops of any one locality were compared with those from the same locality during these successive years. This procedure permitted an absolutely fair comparison by which similarities or differences in the properties of the oils could be easily followed and fluctuations readily noted.

The usual method of steam distillation was applied for the extraction of the volatile oils from the various samples of hops. The conditions of distillation were practically identical in all cases, each sample being distilled until no more oil was noticeable. The California hops were from Perkins, Cosumne, Ukiah, and Wheatland. The Oregon samples were from Independence, the Washington samples from Chehalis, and the New York samples from near Waterville. All were representative samples of commercial sulphured hops. The imported hops were from Saaz, Bohemia.

THE YIELDS OF OIL FROM VARIOUS HOPS.

The yields of oil from various hops during the four successive seasons are given in the following table:

Yields of Volatile Oil from Various Hops During the Years 1906 to 1909, Inclusive.

Source of Hops.	1906	1907	1908	1909	Average.
	Percent.	Percent.	Percent.	Percent.	Percent.
California:					
Perkins	.....	0.2	0.38	0.43	0.336
Cosumne	.....	0.32	0.24	0.42	0.326
Ukiah	.....	0.23	0.53	0.28	0.346
Wheatland	.....	0.21	0.20	0.44	0.283
Oregon	0.34	0.20	0.32	0.30	0.290
New York	0.32	0.16	0.14	0.15	0.192
Washington	.....	.....	0.36	0.38	0.370
Imported (Saaz)	0.45	0.32	0.23	0.24	0.310

Considerable variation exists in the yields of oil from the different California hops, not only among the different samples of any one season, but also among the same hops during successive seasons. The average yield of oil from the California hops during the seasons recorded in the table was 0.32 percent.

The Oregon hops which were distilled during the four successive years showed an average oil content of 0.29 percent, which is a trifle less than the average California sample.

The New York hops with an average during the four years of 0.192 percent of oil were noticeably lower in oil content than any of the other hops distilled.

The Washington hops which were distilled only during two seasons appear to possess the highest percentage of oil, the average being 0.37 percent.

The imported hops distilled from the crops of 1906, 1907, 1908, and 1909, showed an average yield of 0.31 percent of oil, considerable change appearing from season to season.

This variability of the oil content may be ascribed to varying conditions of climate and soil as well as to ripeness and drying of the hops, which would affect the formation of the oil in the plant. Slight differences in yield of oil would not necessarily influence the quality since the same proportion of odoriferous constituents may still be present.

PHYSICAL PROPERTIES OF THE VARIOUS HOP OILS.

The physical properties of the oils permit a somewhat better means of comparison. The properties of color, odor and taste, which are apt to disclose only slight differences, are not discussed. The specific gravity, refractive power and solubility, each of which can be accurately measured, are of much greater importance, although even these properties are usually entirely inadequate for detecting any constant differences in the oils. In all cases the oils were too dark to permit making determination of the optical rotation which is often useful in detecting certain differences in composition. The following tabulations show the differences in the physical properties of the various hop oils distilled during the seasons 1907, 1908, and 1909:

Physical Properties of Various Hop Oils Distilled During Several Successive Seasons.

Specific Gravity at 20° C.

Source of Hops.	1907 Crop.	1908 Crop.	1909 Crop.
California:			
Perkins	0.821	0.838	0.8316
Cosumne	0.821	0.8395**	0.842
Ukiah	0.821	0.831**	0.839**
Wheatland	0.828	0.8443	0.8358
Oregon	0.8343	0.838	0.8433
New York	0.859*	0.834*	0.8747*
Washington	.....	0.850	0.8464
Imported (Saaz)	0.852*	0.821*	0.858*

* Specific Gravity at 24° C.
** Specific Gravity at 23° C.

Index of Refraction at 20° C.

Source of Hops.	1907 Crop.	1908 Crop.	1909 Crop.
California:			
Perkins	1.4838	1.4783	1.4716
Cosumne	1.4825	1.4724	1.4733
Ukiah	1.4890	1.4737	1.4718
Wheatland	1.4870	1.4753	1.4743
Oregon	1.4802	1.4730	1.4705
New York	1.4804	1.4756	1.4800
Washington	.....	1.4763	1.4734
Imported (Saaz)	1.4905	1.4852	1.4829

*Solubility.**

(Amount of Oil Dissolved in 3 Volumes of 94 percent alcohol.)

Source of Hops.	1907 Crop.	1908 Crop.	1909 Crop.
California:			
Perkins	0.55 volume oil, turbid; yellowish residue.	0.7 volume oil, turbid.	0.8 volume of oil.
Cosumne	0.5 volume of oil with whitish residue.	0.85 volume of oil, brownish residue.	0.8 volume oil.
Ukiah	0.35 volume oil, slight turbidity.	0.85 volume oil, turbid	0.95 volume oil. slightly turbid with reddish residue.
Wheatland	0.35 volume oil, yellowish residue.	0.75 volume oil, brown residue.	0.7 volume oil.
Oregon	0.65 volume oil, turbid, yellow residue.	0.9 volume oil.	1 volume oil.
New York	0.85 volume oil, brown residue.	0.85 volume oil.	0.8 volume oil, light brown residue.
Washington	.....	0.85 volume oil, turbid.	0.9 volume oil.
Imported (Saaz)	0.75 volume oil, slightly turbid.	0.5 volume oil, yellowish viscous residue.	0.75 volume oil. slightly turbid. Dark brown viscous residue.

*Solubility of 1907 crop determined after two years; 1908 crop determined after one year.

The densities of the California oils bore a close relationship during individual seasons, differing somewhat from season to season. This would seem to indicate that the approximate composition during any one season was about the same in the several oils. The oils with the highest general specific gravity were those from New York hops, which averaged 0.8554 at 24° C. The Washington, imported, Oregon, and California oils followed in order. It is generally acknowledged that the specific gravity is modified by the composition of the oil but it is doubtful whether the differences noted above would cause any remarkable change in the quality of the oil. A high specific gravity would usually be accompanied by a larger percentage of high-boiling constituents and vice versa.

From the table it will be observed that the oils from imported hops possess higher refractive indices than any of the other oils. This again may be due to the presence of a somewhat higher percentage of highly refractive constituents in these oils. The refraction of the oils from the 1907 crop was higher in most cases than that of the two following years, probably because the constants of the oils from this crop were not determined until 1909, showing that a change had taken place in the oils while aging.

The solubility of hop oil is influenced considerably by the percentage of terpenes and sesqui-terpenes present, the presence of which tend to decrease the solubility in alcohol, while high content of oxygenated compounds increases it. Owing to the preponderance of the former in hop oils and the difficulty thereby encountered in obtaining comparative results, a deviation was made from the usual method for determining solubility. One volume of oil was thoroughly shaken with three volumes of 94 percent alcohol in a graduated cylinder after which the resinous insoluble matter was centrifuged. The amount of insoluble matter could then be easily read on the bottom of the cylinder and the amount of dissolved material readily calculated.

Apparently the most soluble oil among the number was the oil from Oregon

hops of the 1909 crop, one volume of this oil dissolving completely in three volumes of 94 percent alcohol, the oil from the 1908 crop being almost as soluble. The Washington and New York oils from the crops of 1908 and 1909 were slightly less soluble than the Oregon oils. The California oils of these two seasons were a trifle less soluble than those from Washington and New York hops, while the imported oils appeared to be the least soluble.

The much lower solubility of the 1907 oils was due to the fact that the determinations were not made until two years after distillation. Although the oils had been kept in well-filled bottles and well-protected from light, decomposition had ensued which resulted in the formation of less soluble constituents thus decreasing the solubility of the oils. This plainly shows the effect of age on the solubility of the oils.

From the results obtained, it would appear that the oils with the highest solubility probably contained a larger percentage of oxygenated compounds and a lower percentage of terpenic compounds than the less soluble oils.

CHEMICAL PROPERTIES OF THE VARIOUS HOP OILS.

In order to make a better comparison of the several oils with regard to their aromatic quality, determinations were made of the acid, ester and saponification numbers.

A number of factors may tend to influence the acid value. Freshly distilled oils are in most instances low in free acidity, while old oils or oils distilled from old material usually possess a larger quantity of free acids. Improper conditions of drying and storing have a tendency to cause changes to take place which result in the formation of free acids and thereby increase the acid numbers.

As previously stated, the ester values of oils are subject to marked changes due to conditions of climate, soil, etc. This value in hop oils may also be affected by conditions under which the material is dried and stored. The stage of growth and development of the plant as influenced by geographical location may also be a strong factor in modifying the ester content.

The saponification number being the sum of the acid and ester numbers should indicate much the same differences, as shown by the ester numbers. A determination of free alcohols in hop oils was not feasible because of the inability to acetylize the oil quantitatively.

The acid, ester and saponification numbers of the oils from the American and foreign hops are recorded as follows:

The Acid, Ester and Saponification Numbers of Hop Oils Distilled During Several Seasons.

Acid Numbers.

Source of Hops.	1906	1907	1908	1909	1910	Average
California:						
Perkins	.....	0	1.5	1.1	.....	0.86
Cosumne	.....	0	2.4	2.9	.....	1.76
Ukiah	.....	0	1.1	1.8	.....	0.96
Wheatland	.....	2.3	2.0	1.4	.....	1.9
Oregon	5.5	1.6	1.0	2.8	.....	2.7
New York	4.8	3.6	2.1	2.5	.....	3.25
Washington	.....	.....	1.0	1.5	.....	1.25
Imported (Saaz)	1.5	1.5	1.0	3.0	3.1	2.02

Ester Numbers.

Source of Hops.	1906	1907	1908	1909	1910	Average
California:						
Perkins	.....	42	47	47.1	.....	45.5
Cosumne	.....	45	46	51	.....	47.3
Ukiah	.....	40.8	44	51	.....	45.2
Wheatland	.....	50	45.5	41	.....	45.5
Oregon	72	57	50.2	56	.....	58.8
New York	44	61	47	51.8	.....	50.9
Washington	.....	.....	51.8	53.8	.....	52.8
Imported (Saaz)	12.6	20	36	28.6	20.4	23.5

Saponification Numbers.

Source of Hops.	1906	1907	1908	.909	1910	Average
California:						
Perkins	.....	42	48.5	48.2	.....	46.2
Cosumne	.....	45	48.4	53.9	.....	49.1
Ukiah	.....	40.8	45.1	52.8	.....	46.2
Wheatland	.....	52.3	47.5	42.4	.....	47.4
Oregon	77.5	58.6	51.2	58.8	.....	61.5
New York	48.8	64.6	49.1	54.3	.....	54.2
Washington	.....	.....	52.8	55.3	.....	54.0
Imported (Saaz)	14.1	21.5	37	31.6	23.5	21.5

The oils in order of their average acidity were as follows: New York, Oregon, imported, California, and Washington. In every instance the New York oils showed comparatively high acidity. The average acidity of the New York and Oregon oils was probably somewhat high as it was considerably augmented by the high acid number of the oil from 1906 crop which was distilled from hops which were not fresh as were those from 1907, 1908, and 1909 crops. The oils with lowest acidity were from California and Washington hops, while the imported hops occupied an intermediate position.

The ester numbers revealed most striking similarities and dissimilarities, not only during one season, but for several successive seasons. It was to be expected that the oils from the hops during any one season would show differences but that these same differences should appear during three and four and even five successive seasons was most surprising.

The oils from the imported hops were conspicuous because of the fact that the data for the several seasons showed the ester content to be only about one-half as great as the ester content of the oils from the California, Oregon, Washington and New York hops. Besides the samples recorded, a cold storage sample of Saaz hops of the 1906 crop distilled one year later gave an oil with an ester number of 24. Three samples of imported hops of the 1910 crop, namely, Dauber, Auscher and Oesterreich Gewächs hops, possessed the ester numbers 15.7, 21.3, and 18, respectively. In all nine samples of imported hops from five seasons gave oils with uniformly lower ester content than American hops.

The close relationship of the ester numbers of the California oils during the seasons of 1907, 1908 and 1909, is very evident. The general average ester

number of the California oils was 45.5, as compared with 50.9 for New York, 52.8 for Washington, 58.8 for Oregon, and 23.5 for the imported.

In case of the foreign oils the ester numbers, which are a measure of the odorous constituents, would seem to point to consistently lower content of these compounds.

The saponification numbers which represent the total acids and esters in the oils presented practically the same constant differences and similarities brought out by comparison of the ester numbers.

While it is not known whether the ester numbers would continue lower indefinitely in case of the foreign oils, it may be assumed that such would be the case, since the authentic samples distilled during five seasons showed abnormally low values as compared with the American oils. In a like manner also it may be assumed that the high ester numbers of the American oils would continue indefinitely since they were quite remarkably constant during the seasons in which the experiments were carried on.

THE RELATION OF THE VOLATILE OIL TO THE SOURCE OF THE HOPS.

A comparison of the fractions resulting from the fractionation of each of the above oils both with regard to physical and chemical constants brought out the same relationships as were shown to exist in the oils themselves. It is, of course, impossible to discuss these results in detail in the short space of this paper. However, from the data presented it is clearly evident that the geographical source of hops has a pronounced effect upon the volatile oil and particularly upon the ester content. The differences noted in the oils appear to be fairly constant from season to season, not only in the physical properties but also in the more important chemical properties. Not only do hops of foreign origin produce oils noticeably dissimilar in some of their properties from the American oils, but hops grown even in separated sections of the United States yield oils with more or less constant differences from year to year. In general, it may be stated with some degree of certainty that the geographical source of hops exerts a decided influence upon the composition of the oils, especially as regards the ester content. Furthermore, it seems highly probable that the geographical source of hops may be indicated by the ester numbers of the oil distilled from the hops since the experiments have shown that the ester numbers of the oils from hops of any particular source or season are very similar.